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Vol. 205 MAY, 1928 No. 5

ARE ELECTRONS WAVES? *

BY

C. J. DAVISSON, Ph.D.

Bell Telephone Laboratories, Inc.

I MUST tell you to begin with that Dr. Germer and I are keenly aware of the very great compliment you have paid us in asking me to come here this evening and describe to you our experiments with electrons. It is a compliment which we appreciate very much indeed.

The title which I have chosen for my address, "Are electrons waves?," suggests that some doubt has arisen in regard to the nature of electrons. And this is true. The fact is that circumstances have been found in which electrons try to make out that they are not particles at all, but are instead waves.

As an example of this perverseness I shall describe a simple type of experiment that Dr. Germer and I have been making for the past several months. We direct a narrow stream of electrons against the face of a nickel crystal, and observe that under certain conditions a sharply defined stream of electrons leaves the crystal in the direction of regular reflection—angle of reflection equal to angle of incidence.

At first thought there may seem to be nothing so very strange in this. Why should not electrons be regularly reflected from a metal surface? We know that Newton and

* Presented at the Stated Meeting held Wednesday, March 21, 1928.

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other adherents of the corpuscular theory of light were not embarrassed by the fact that light is regularly reflected from a plane mirror. The phenomenon is one that they could explain quite easily. It is well known that in an elastic encounter between a particle and a plane surface the particle rebounds from the surface in the direction of regular reflection —hence the regular reflections of light on the corpuscular theory, and why not also the regular reflection of electrons?

Well, the adherents of the corpuscular theory of light had certain advantages over us in picturing reflection in this way. They had not committed themselves in regard to the size of the light corpuscle, and they knew nothing about the structure of metallic surfaces. We have reasons for believing that the electron is about 10^{-13} cm. in diameter. We know that atoms have diameters of the order 10^{-8} cm. and we know also that the least distance between atoms in the nickel crystal is 2.48×10^{-8} cm. If we take 10^{-13} cm. as a unit of length, then the diameter of the electron is one of these units, the diameter of the nickel atom is one hundred thousand, and the least distance between atoms in the nickel crystal is nearly 250,000.

The difficulty of picturing the regular reflection of particles as small as electrons from a surface made up of bodies as large as atoms is at once evident. If we were to fire a load of bird shot against a pyramid of cannon balls, we should not expect to find a little cloud of shot moving off in the direction of the regular reflection from the face of the pyramid. A surface made up of cannon balls is much too coarse grained to serve as a regular reflector for particles as small as bird shot.

The analogy is not such a good one really, for we do not think of electrons rebounding from the surface of an atom in the way that shot rebound from a cannon ball. We have been accustomed to think of the atom as rather like the solar system—a massive nuclear sun surrounded by planetary electrons moving in closed orbits. On this view the electron which strikes into a metal surface is like a comet plunging into a region rather densely packed with solar systems.

There is a certain small probability, or at least there might seem to be, that the electron will strike into an atom in or near the surface of the metal, be swung about comet-wise, and sent flying out of the metal without loss of energy. The direction taken by such an electron as it leaves the metal should be a matter of private treaty between the electron and the individual atom. One does not see how the neighboring atoms could have any voice in the matter. And yet we find that the high-speed scattered electrons have a preference for moving off in the direction of regular reflection, a direction which is related to the plane of the surface. Three atoms at least are required to fix this plane, so that the direction taken by the electron is determined not by one atom, but by three atoms at least.

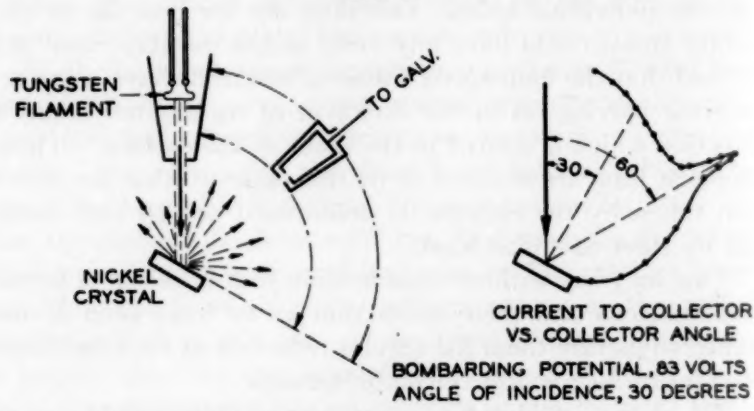
One may say without qualification that in terms of atoms and electrons and their interaction as we have been accustomed to picture them the regular reflection of electrons from a metal surface is quite incomprehensible.

Of course, if electrons were waves there would be no difficulty. We think we understand the regular reflection of light and of x-rays—and we should understand the reflection of electrons as well if electrons were only waves instead of particles. This observation though true does not seem a particularly valuable one. It is rather as if one were to see a rabbit climbing a tree, and were to say, "Well, that is rather a strange thing for a rabbit to be doing, but after all there is really nothing to get excited about. Cats climb trees —so that, if the rabbit were only a cat, we would understand its behavior perfectly." Of course, the explanation might be that what we took to be a rabbit was not a rabbit at all, but was actually a cat. Is it possible that we are mistaken about electrons? Is it possible that we have been wrong all this time in supposing that they are particles, and that actually they are waves? Well, I do not need to enumerate to you the many reasons we have for believing—I may say for knowing—that electrons are actually particles.

As if these reasons were not numerous enough—the very

method by which we detect the regular reflected beam supplies still another. The regularly reflected beam is found by moving a small bucket about in front of the crystal and observing that more electrons are caught when the bucket stands in the direction of regular reflection than in any other.

FIG. 1.



Experimental arrangement for investigating the scattering of electrons by a crystal, and a typical curve showing beam of regularly reflected electrons.

A diagram of the experimental arrangement is shown in Fig. 1.

This arrangement of filament and box is an electron gun which supplies us with a steady stream of electrons. The speed of the electrons is under our control and can be given any desired value by maintaining a suitable potential difference between the filament and the box. This stream is directed against the crystal, and electrons of various speeds move off in all directions from the bombarded area.

To find how many are moving off in different directions we move the collector, which is really a bucket, and find how many electrons we catch in different positions. To get into the inner box an electron must pass through the opening in the outer box. Those that succeed in doing this flow off through a galvanometer, and the deflection of the galvanometer is a measure of the rate at which they are being caught.

The method is one which with some slight modification might be used to find how bird shot are scattered by a pile of cannon balls. It is not in principle a method we would employ to investigate the scattering of light or of x-rays.

In making observations the collector is moved about in front of the crystal, and curves are constructed showing the current received by the collector as a function of angle.

Such a curve for angle of incidence 30 degrees and for bombarding potential 83 volts is shown on the right, and you see the sharp spur protruding from the curve exactly in the direction of regular reflection. You will want to know about the electrons leaving the crystal in other directions. Well, those are, almost all of them, low-speed secondary electrons—while the electrons responsible for this spur have, most of them, the same speed as the incident electrons.

There is no doubt that the incident electrons recognize the surface of the crystal, and prefer to move off in the direction of regular reflection.

The next experiment I shall describe is more simple even than the first. We direct a stream of electrons against a target of ordinary nickel—a target made up of many small crystals instead of one large one—and we never under any circumstances find any indication of regular reflection. Electrons are not regularly reflected from a target of ordinary polycrystalline nickel.

It seems curious that electrons should be reflected only from a crystal-face—and then we remember that this is true also of x-rays. X-rays may be regularly reflected from the face of a crystal, but not from a polycrystalline mirror. The difference between light and x-rays in this respect is due, as we know, to a difference in order of wave-lengths. The lengths of light waves are great compared to the distance between atoms in solids while the x-ray wave-lengths are comparable with these distances.

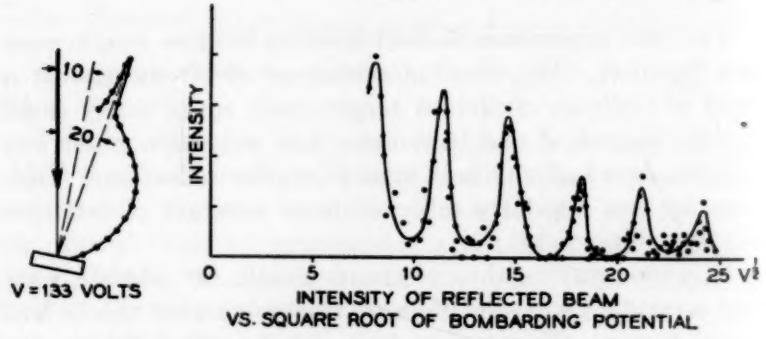
We may say then that both of these results—the regular reflection of electrons from a crystal-face and the absence of

such reflections from a polycrystalline surface—would be comprehensible if electrons were trains of waves of wave-lengths comparable to distances between atoms in solids.

Now it will be remembered that x-ray reflection is characterized by a marked selectivity. If a beam of monochromatic x-rays is directed against a crystal face, the intensity of the beam reflected at a certain angle is very nearly zero unless the wave-length of the beam happens to lie at, or very near to, one or another of a series of discrete values. It is as if we had a mirror which would reflect red light of a certain wave-length and also blue light of a certain wave-length, but which would not reflect light of any of the intermediate wave-lengths.

This suggests an interesting experiment. If electrons resemble x-rays in being reflected from a crystal, but not from a polycrystalline surface, do they also resemble x-rays in exhibiting selective reflection? We might expect, for example,

FIG. 2.



Showing selectivity of electron reflection—angle of incidence 10 degrees.

that if electron reflection is really like x-ray reflection it would be selective in speed of bombardment. Well, the astonishing thing is that it *is* selective in speed. When we measure the intensity of the reflected beam as a function of speed of bombardment, we find that it passes through one maximum after another as the speed is increased. A curve exhibiting this behavior is shown in Fig. 2.

The ordinate is the intensity of the reflected beam, and the abscissa is the square root of the bombarding potential, which is proportional to the speed of the electrons in the incident beam. These observations are for angle of incidence ten degrees, and the curve on the left shows the reflected beam at the second maximum of the intensity curve.

Now the selective reflection of x-rays is a phenomenon which is very thoroughly understood. In explaining it we make very definite and explicit use of the idea that x-rays are waves. In fact, the phenomenon supplies us with our most reliable means of measuring x-ray wave-lengths. It is very significant indeed that electron reflection resembles x-ray reflection in this particular respect.

FIG. 3.

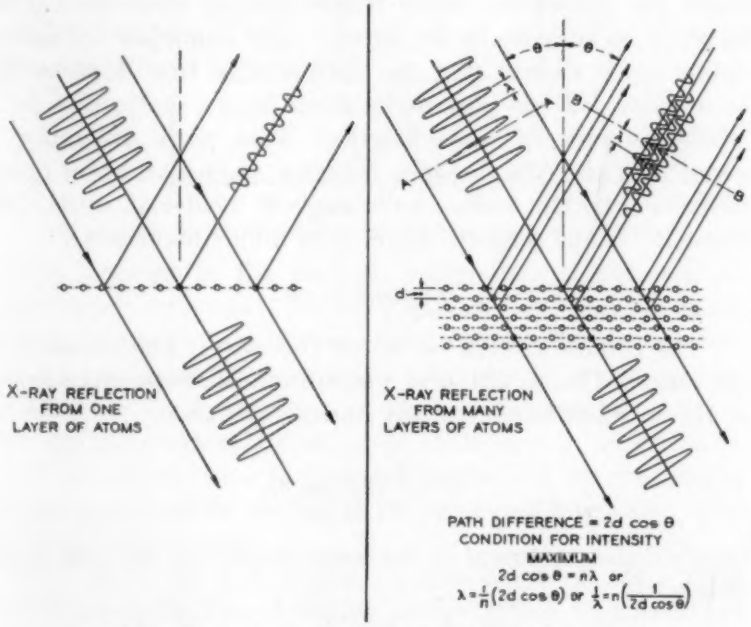


Diagram illustrating the selective reflection of x-rays from a crystal.

I shall take just a few minutes to review with you the theory of x-ray crystal reflection and the explanation of the selectivity.

When a beam of x-rays is incident upon a single layer of atoms as illustrated on the left in Fig. 3, the beam passes through the layer with only very slight diminution in its intensity. It does, however, set up forced vibrations in the atoms which it irradiates, and these send forth trains of spherical waves which are related in phase, and which combine to form a beam of waves moving off from the plane in the direction of regular reflection. The reflection of x-rays from a single layer of atoms is not selective.

Selectivity develops when reflection occurs from a number of parallel layers of atoms such as we have in a crystal. The case is illustrated in the figure on the right. The reflection beams proceeding from the different layers are superposed and the resultant beam exhibits a strong intensity maximum when the elementary wave trains proceed from the crystal in phase as they do in the figure. The condition for such a maximum is clearly that the path-lengths from a plane AA to a plane BB via successive atom layers shall differ by a whole number of wave-lengths. This path difference is given by twice the distance between successive atom layers multiplied by the cosine of the angle of incidence, so that the intensity of the reflected beam is at a maximum when

$$2d \cos \theta = n\lambda.$$

The condition may be stated this way: The intensity of the reflected beam will be at a maximum when the wave-length of the incident beam has any one of the values

$$\lambda = \frac{1}{n}(2d \cos \theta),$$

or when the reciprocal of the wave-length has any one of the values

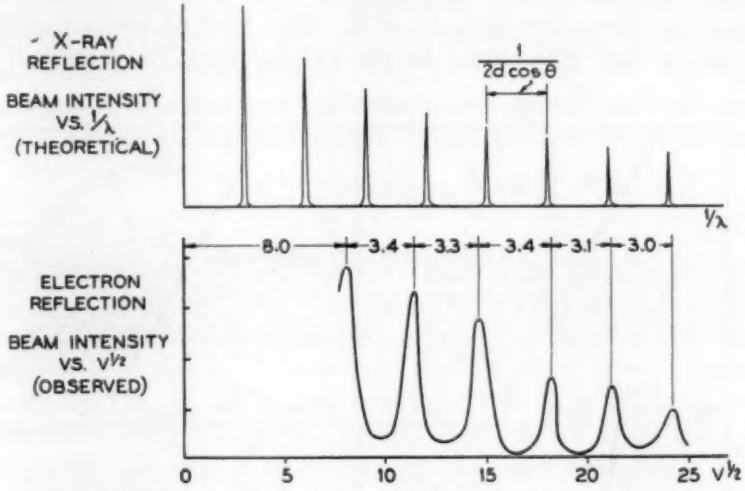
$$\frac{1}{\lambda} = n \frac{1}{2d \cos \theta}.$$

Thus, if we plot the intensity of the reflected beam against the reciprocal of the wave-length, we should obtain a curve

characterized by a series of equally spaced maxima. What we should find is illustrated by the curve at the top of Fig. 4.

In the lower half of the figure I show again, for comparison, the intensity of the electron reflection beam as a function of $V^{1/2}$, the square root of the bombarding potential.

FIG. 4.



Showing the selective reflection of x-rays, and the selective reflection of electrons.

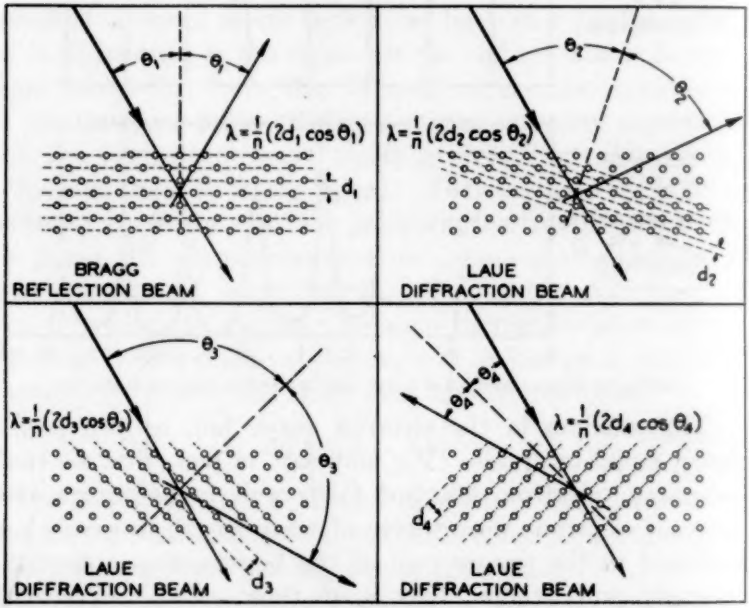
The maxima in the electron curve fall, as you see, at almost equal intervals. We may say, in fact, that we could understand electron reflection fairly well, including its selectivity, if electrons were waves of wave-length inversely proportional to the square root of the bombarding potential—inversely proportional, that is, to their speed. Apparently this would not be a perfect interpretation, for the maxima in the electron curve do not fall at exactly equal intervals. But it would do fairly well.

Well, here we are almost on the point of calculating electron wave-lengths—knowing perfectly well that electrons are particles. It is time for us to take some definite stand in regard to this matter, and I propose that we hold to our knowledge that electrons are particles, but admit that they are behaving as if they were waves—at least, that we can

describe what we observe by pretending that they are waves, and that we do not see how the observations can be described in terms of particles. We take this point of view, and see how long it can be maintained.

Now, when x-rays are scattered by a crystal, beams issue from the crystal not only in the direction of regular reflection, but in other directions as well. One way of understanding this is that the atoms in the crystal may be regarded as

FIG. 5.



Reflection of x-rays from various planes of atoms in a crystal—illustrating the formation of Laue diffraction beams.

arranged in planes parallel to the surface of the crystal, but that they may also be regarded as arranged in planes that are not parallel to the surface—and that as far as the x-rays are concerned one set of atom planes is just as good as another. The situation is illustrated in Fig. 5.

If a beam of x-rays is incident upon a crystal face at angle θ_1, a regularly reflected beam issues from the crystal when the wave-length has any of the values

$$\lambda = \frac{1}{n}(2d_1 \cos \theta_1).$$

This beam is due to regular reflection from atom planes parallel to the surface and is ordinarily referred to as the Bragg reflection beam. But the atoms may also be regarded as arranged in other sets of planes as indicated in the other figures, and these also give rise to reflected beams. We find, for example, a beam issuing from the crystal in the direction of regular reflection from the atom planes shown in the second figure at the top when the wave-length has any of the values

$$\lambda = \frac{1}{n}(2d_2 \cos \theta_2).$$

Such beams are ordinarily known as Laue diffraction beams.

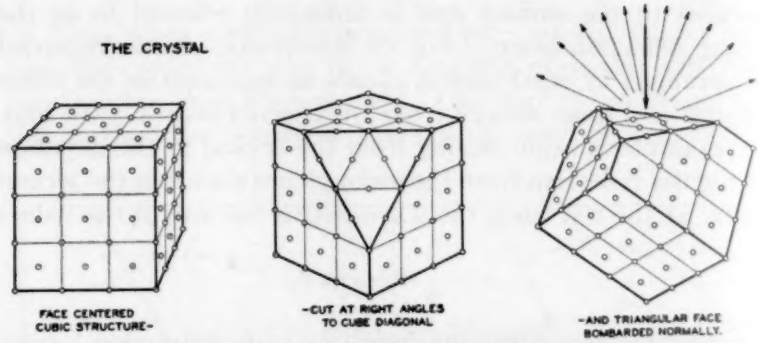
We have seen that electrons resemble x-rays in being regularly reflected from the face of a crystal and in exhibiting selectivity. The question now is, do they also resemble x-rays in giving rise to diffraction beams. Well, as it happens, we observed these diffraction beams first—more than a year before we got around to looking for the reflection beams.

It is not going to be so easy to describe these diffraction beams as it has been to describe the reflection beams; there are differences between the characteristics of the x-ray and electron diffraction beams from which one might think that after all electrons are really not so very good at passing themselves off as waves. And yet we will find that these differences can be explained in a reasonable way, and that the diffraction data lead to quite definite values of electron wave-lengths. In describing these experiments I shall try first to give you a clear idea of the conditions under which the observations were made, next what would have been observed had the experiments been made with x-rays, and finally what was actually observed with electrons.

To begin with we shall need to understand the arrangement of atoms in the nickel crystal. Nickel forms crystals of the face centered cubic type. The unit of structure is a cube—3.51 Å. on the edge—with an atom at each corner

and one in the center of each face. The large cube on the left in Fig. 6 is built up of 27 of these unit cubes. The only

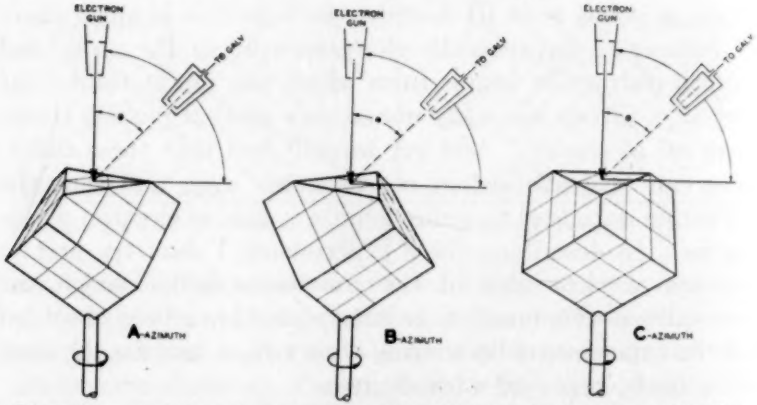
FIG. 6.


THE CRYSTAL
FACE CENTERED CUBIC STRUCTURE-
-CUT AT RIGHT ANGLES TO CUBE DIAGONAL
-AND TRIANGULAR FACE BOMBARDED NORMALLY.

Schematic representations of the face centered cubic crystal of nickel.

atoms shown are those in the surface of the large cube. Henceforth I shall use this large cube as a symbol to represent the nickel crystal with which we began our experiments. We first cut through this structure at right angles to one of the cube diagonals, forming the triangular faces shown in the

FIG. 7.



Schematic representations of experimental arrangement for investigating electron diffraction.

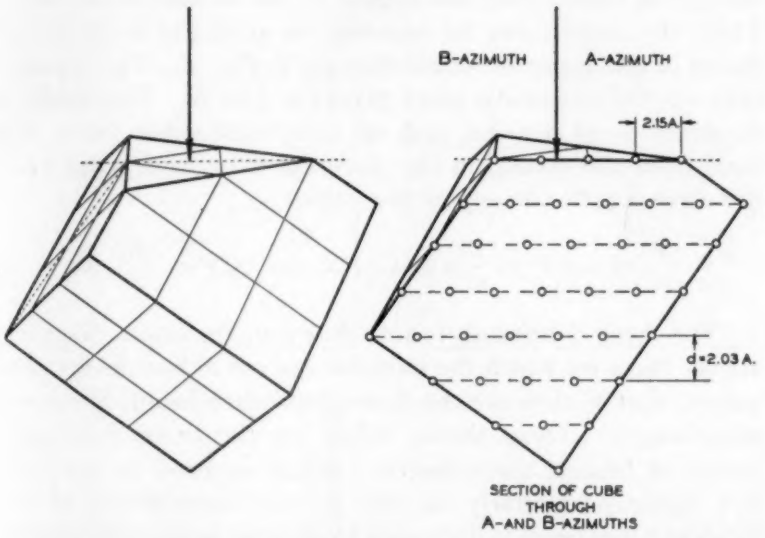
central figure. A beam of electrons was then directed against this face at normal incidence, as indicated in the figure on the right, and measurements were made of the number of electrons

leaving the crystal as a function of direction and of speed of bombardment.

The experimental arrangements for making these measurements are indicated in Fig. 7. The collector could be moved about in a single plane—the plane of the drawing and the crystal could be rotated about a vertical axis so that any azimuth of the crystal could be brought into the plane of rotation of the collector.

It is clear that the crystal has a three-fold symmetry. If we find a beam issuing from the crystal when one of the apexes of the triangle is in the plane of the collector, we will expect, of course, to find a similar beam when the crystal

FIG. 8.



has been turned through 120° to bring another of the apexes into the collector plane, and again when it has been turned through 240 degrees. We will call the azimuths of the crystal that include the apexes of the triangle the *A*-azimuths; those including the midpoints of the sides of the triangles the *B*-azimuths; and those parallel to the sides of the triangle the *C*-azimuths.

In Fig. 8 we show a cross section of the crystal through the plane of the A–B-azimuths. The circles represent lines of atoms extending through the crystal at right angles to this plane. The crystal may be regarded as built up of planes of atoms lying parallel to the surface of the crystal. The distance between these planes is 2.03 Å., and the distance between the lines of atoms in each plane is 2.15 Å. It will be noticed that the lines of atoms in a given plane are not directly below the lines of atoms in the next higher plane, but are shifted to the right by an amount equal to one-third of the distance between lines.

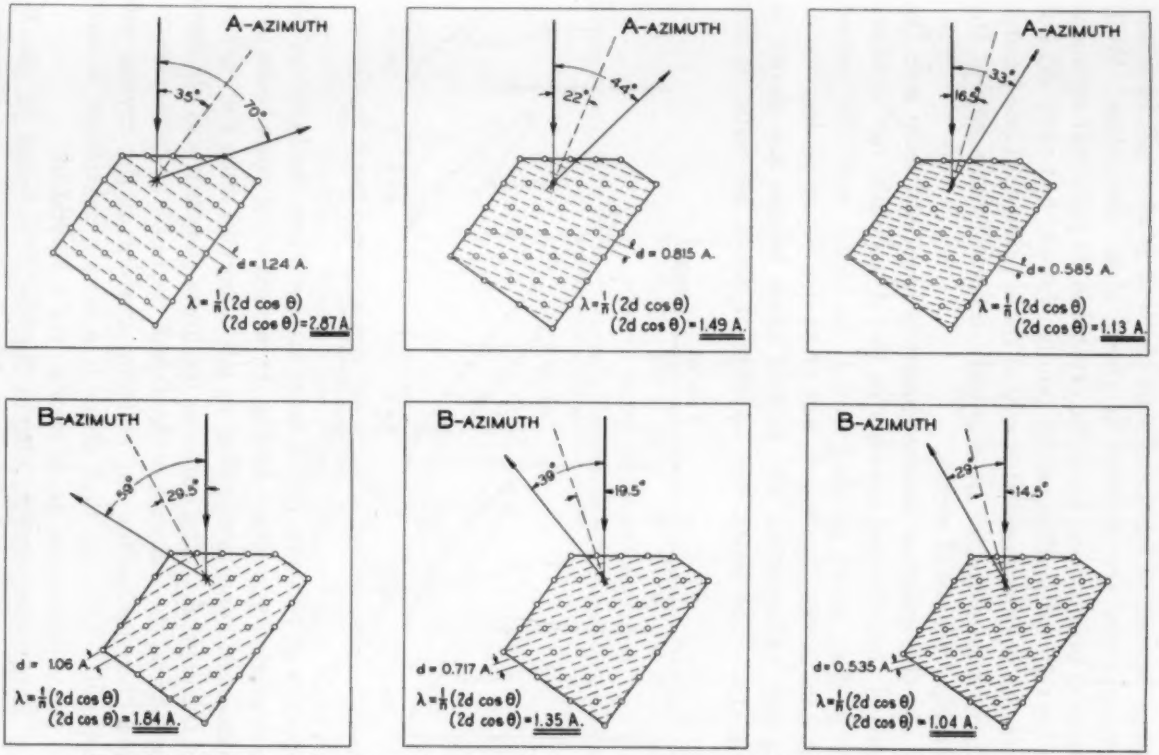
The crystal is now sufficiently specified to enable us to calculate the wave-lengths and positions of all the x-ray diffraction beams that can appear in the A- and B-azimuths. Thus, the atoms may be regarded as arranged in planes as shown in the upper left-hand diagram in Fig. 9. The distance between the successive atom planes is 1.24 Å. The angle of incidence is 35 degrees, and an x-ray diffraction beam will issue from the crystal in the direction $\theta' = 70$ degrees when the wave-length has any of the values

$$\frac{1}{n}(2d \cos \theta) = \frac{1}{n}(2 \times 1.24 \times \cos 35°) = \frac{2.87}{n} \text{ Å.}$$

The three A-azimuth beams shown in the upper diagrams are the three for which the modulus $(2d \cos \theta)$ has the greatest values, that is, they are the three A-azimuth beams of longest wave-length. Those shown below are the three B-azimuth beams of longest wave-length. What we need to get from this figure particularly is that as the wave-length of the incident x-ray beam is decreased from some large value diffraction beams appear in the following order: first, a beam at 70 degrees in the A-azimuth; next, a beam at 59 degrees in the B-azimuth; then, a beam at 44 degrees in the A-azimuth, followed by a B-azimuth beam at 39 degrees.

This is what would occur if the incident beam were a beam of x-rays—and from what we have seen of the regular reflection of electrons from the atom planes lying parallel to

FIG. 9.

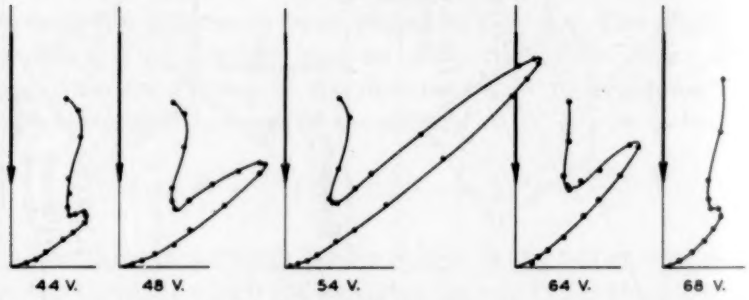


The principal diffraction beams that would appear in the *A*- and *B*-azimuths if the incident beam were a beam of x-rays.

the surface it seems not unreasonable to expect that at particular speeds of bombardment electron beams will be found issuing from the crystal in these same directions. Well, electron beams issue from the crystal in its principal azimuths at certain critical speeds of bombardment, but they do not coincide in directions with any of these principal Laue beams. They appear not to be regularly reflected from any of the principal planes of atoms.

As the speed of bombardment is increased from zero the first of these beams appears in the *A*-azimuth, not however at 70 deg. or at 44 deg. but at 50 deg.; and the second appears in the *B*-azimuth, not at 59 deg. or at 39 deg. but at 44 deg. Curves for the first of these beams are shown in Fig. 10. The beam first appears at about 40 volts; it dis-

FIG. 10.

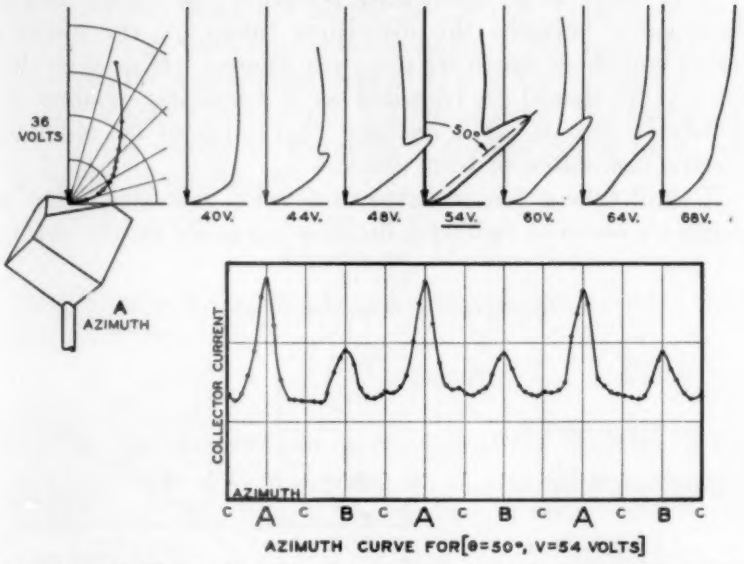


Showing the growth and decay of the "54-volt" electron diffraction beam in the *A*-azimuth—surface of crystal clean.

appears at 70 volts, and is most intense when the bombarding potential is 54 volts. In Fig. 11 we have the same beam in a weakened condition owing to gas adsorbed onto the surface of the crystal. The curve in the lower diagram was obtained by setting the collector in the axis of the beam at its maximum, and then measuring the collector current as the crystal was rotated. You see that there is a strong maximum in each of the *A*-azimuths, as, of course, there should be.

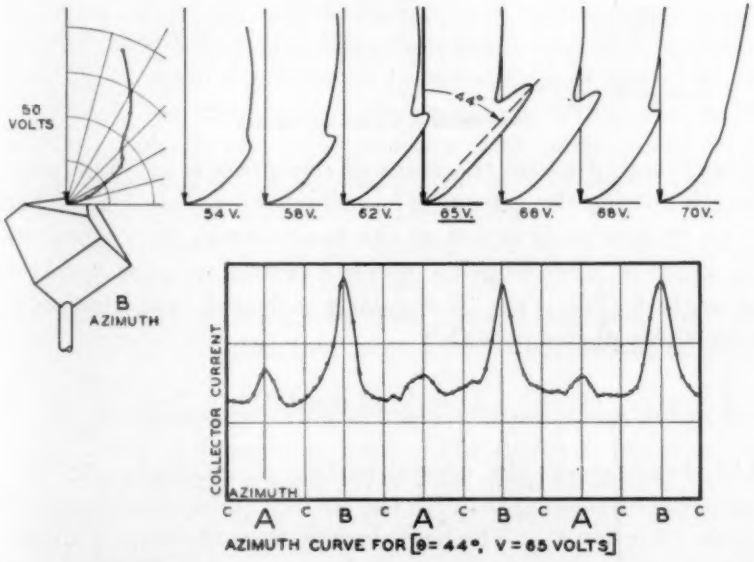
The corresponding curves for the first beam in the *B*-azimuth are shown in Fig. 12. Maximum intensity is attained at 65 volts, with the beam at 44 deg.

FIG. 11.



Showing "54-volt" diffraction beam weakened by contamination of the crystal surface—azimuth curve showing maxima in *A*-azimuths.

FIG. 12.



Growth and decay of the "65-volt" beam in the *B*-azimuth—surface of crystal contaminated by gas. Azimuth curve showing maxima in *B*-azimuths.

Now there is an interesting possibility in regard to this discrepancy between the directions taken by the electron beams and those taken by the x-ray beams. It may be that the crystal should be regarded as a refracting medium for electrons—that is, as a medium characterized by an index of refraction different from unity.

I shall take a few minutes to develop this idea. Let us imagine a beam of radiation incident normally on the surface

FIG. 13.

DIFFRACTION BY REFRACTING CRYSTAL

$$\mu = \frac{\lambda}{\lambda'} = \frac{\sin\theta'}{\sin 2\theta}$$

$$\lambda' = \lambda \frac{\sin 2\theta}{\sin\theta'} = \frac{1}{n}(2d\cos\theta)$$

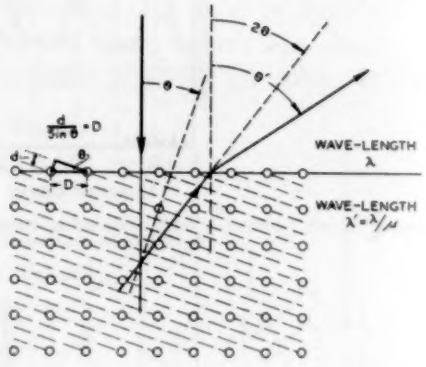
$$\lambda = \frac{1}{n}\left(\frac{2d\cos\theta}{\sin 2\theta}\right)\sin\theta'$$

$$\lambda = \frac{1}{n}\left(\frac{2d\cos\theta}{2\sin\theta\cos\theta}\right)\sin\theta'$$

$$\lambda = \frac{1}{n}\left(\frac{d}{\sin\theta}\right)\sin\theta'$$

But $\quad \frac{d}{\sin\theta} = D$

$$\therefore \quad \underline{\lambda = \frac{1}{n} D \sin\theta'}$$



DERIVATION OF PLANE GRATING FORMULA

of a crystal of which the index of refraction is μ. The wave-length outside the crystal is λ, and inside is $\lambda' = \lambda/\mu$. There is no change in direction as the beam enters the crystal and the beam of wave-length λ' meets a certain set of atom planes at angle θ (Fig. 13). A regularly reflected beam moves off from these planes provided

$$\lambda' = \frac{1}{n}(2d\cos\theta).$$

This beam meets the crystal surface at an angle 2θ, but is refracted on passing through the surface and leaves the crystal in the direction θ'. The beam issuing from the crystal appears not to be regularly reflected from any of the principal atom planes.

And now I am going to ask you to follow through the brief mathematical deduction on the left in Fig. 13 as it leads to an interesting and important relation. We treat electron radiation as if it were light, and write $\mu = \lambda/\lambda' = \sin\theta'/\sin 2\theta$. Solving this for λ', we have $\lambda' = \lambda \sin 2\theta/\sin\theta'$, but by Bragg's law $\lambda' = (2d\cos\theta)/n$. Equating these expressions for λ', and solving for λ, we obtain

$$\lambda = \frac{1}{n}\left(\frac{2d\cos\theta}{\sin 2\theta}\right)\sin\theta'.$$

And writing in $2\sin\theta\cos\theta$ for $\sin 2\theta$ and eliminating $2\cos\theta$, this reduces to

$$\lambda = \frac{1}{n}\left(\frac{d}{\sin\theta}\right)\sin\theta'.$$

But from the construction on the left of the diagram in Fig. 13 we see that $d/\sin\theta$ is equal to D, the distance between adjacent lines of atoms in the surface of the crystal.* We have, therefore,

$$\lambda = \frac{1}{n}D\sin\theta'.$$

This is an extremely useful relation, as it enables us to calculate the wave-length of a diffraction beam (provided we knew its order n) from the distance between lines of atoms in the surface of the crystal and the angle at which the beam emerges. We do not need to know with what set of atom planes a given beam is associated, and neither do we need to know the index of refraction of the crystal.

The idea of regarding the crystal as a refracting medium for electrons is due to Dr. Eckart of the California Institute of Technology, although we had already assumed that the wave-lengths of diffraction beams could be calculated from this formula.

We therefore apply this formula to the electron diffraction beams for which we have data. The distance between the lines of atoms lying normal to the A- and B-azimuths is 2.15 Å. The beam which is observed in the A-azimuth when the

* In general $d/\sin\theta = D/m$, where m represents an integer. The conclusion is unaffected, however, by this circumstance.

bombarding potential is 54 volts lies at $\theta' = 50$ degrees. The wave-length of "54-volt electrons" should then be given by

$$\lambda = \frac{2.15}{n} \sin 50° = \frac{1.65}{n}.$$

But since this is the first beam that appears in the A-azimuth it is certainly a first order beam, and therefore $\lambda = 1.65$ Å. When we make a similar calculation for the 65-volt beam in the B-azimuth, we find $\lambda = 1.50$ Å.

That one can calculate the wave-length of a stream of electrons in a straightforward and simple way seems, of course, very surprising, and yet it is much less surprising today than it would have been, say, five years ago. During the last four or five years there has been a rapidly growing conviction that the principles of mechanics, in their various formulations, as we have known them, are really only first approximations to what we may call the true principles of mechanics. They are remarkably close approximations for most purposes—for the purposes of mechanical engineering and astronomy it is unlikely that they can be improved upon either for convenience or reliability—and yet there is the conviction that classical mechanics is in a sense a degenerate form of the true mechanics, and therefore of limited applicability. It is a first approximation to the true mechanics applicable only in those cases in which the products of the momenta and linear dimensions used in describing the system are large compared to the Planck constant of action h —large, that is, compared to 10^{-26} erg sec. We are to feel no hesitation for example in using classical mechanics in dealing with the mechanics of the solar system; the linear dimensions involved are of the order of the major axes of the orbits of the planets, the momenta involved are the momenta of the planets, and the products of these quantities are enormously great compared to the value of h. On the other hand, we are not to suppose that the approximate form of the true mechanics which is applicable to the solar system is applicable also to a system such as the Bohr atom. Here the products

of linear dimensions and momenta are not large compared to h. They are in fact of the same order as h, and laws of mechanics as we have known them are therefore of no service. They are of limited applicability, and do not apply in this case.

This conviction has grown out of dissatisfaction with the ever-mounting artificiality of the Bohr atom model as means for describing and correlating the data of spectroscopy. It has led to attempts in various quarters to discover or invent a new system of mechanics which will degenerate to our ordinary mechanics in the case of gross systems, but which will be applicable as well and without forcing to systems involving atoms and electrons. One of these attempts was made by L. deBroglie who put forward the idea, a little more than three years ago, that every mechanical phenomenon is in some sense a wave phenomenon—that every problem in mechanics is in a way a problem in optics—that in the rigorous solution of all such problems one must always concern himself with the propagation and interference of waves. This idea has been taken up with great enthusiasm by theoretical physicists, notably by Schroedinger, and has enjoyed a rapid and remarkable development. This development is known as the undulatory or wave theory of mechanics, and it gives promise of being perhaps the sorely needed true mechanics. It is yet in a state of flux—no one, I think, knows what its final form will be. Ideas regarding its form and interpretation are constantly changing, and yet from its inception in the hands of deBroglie to the present time there has persisted the idea that a freely moving particle of momentum (mv) is equivalent to, or has associated with it, a train of waves of wave-length h/mv. Whether the particle is itself a group of waves—whether the waves are to be thought of as real physical waves such as we have supposed light waves to be, or whether the waves are purely analytical—a mathematical convenience only—no one, I think, knows.

The development of this theory has so far been directed almost entirely toward giving us a new picture of the atom, and a new and less arbitrary set of rules for correlating and

interpreting the data of spectroscopy. Not so much attention has been paid to aperiodic phenomena such as we are here concerned with, and yet a few months after we had begun our experiments, but more than a year before we had obtained any of the results I have described, the prediction was made by Elsasser in Germany that evidence for the wave nature of mechanics would be found in the interaction between a stream of electrons and a crystal.

Most of you know already, of course, that the electron wave-lengths obtained by the measurements I have been describing are in good agreement with the values of h/mv of this new theory of mechanics. We have

$$\lambda = h/mv,$$

and for electrons of moderate speeds such as we have used we have also

$$\frac{mv^2}{2} = \frac{Ve}{300},$$

where e represents the charge of the electron in electrostatic units and V the bombarding potential in volts.

Eliminating the velocity v between these equations, we obtain

$$\lambda = \left(\frac{h^2}{me}\right)^{1/2}\left(\frac{150}{V}\right)^{1/2} \text{cm.}$$

The value of $(h^2/me)^{1/2}$ differs from 1×10^{-8} by about 2 parts in a thousand so that to a close approximation

$$\lambda = \left(\frac{150}{V}\right)^{1/2} 10^{-8} \text{ cm.}$$

or

$$= \left(\frac{150}{V^{1/2}}\right)^{1/2} \text{Å.}$$

$$= \frac{12.25}{V^{1/2}}.$$

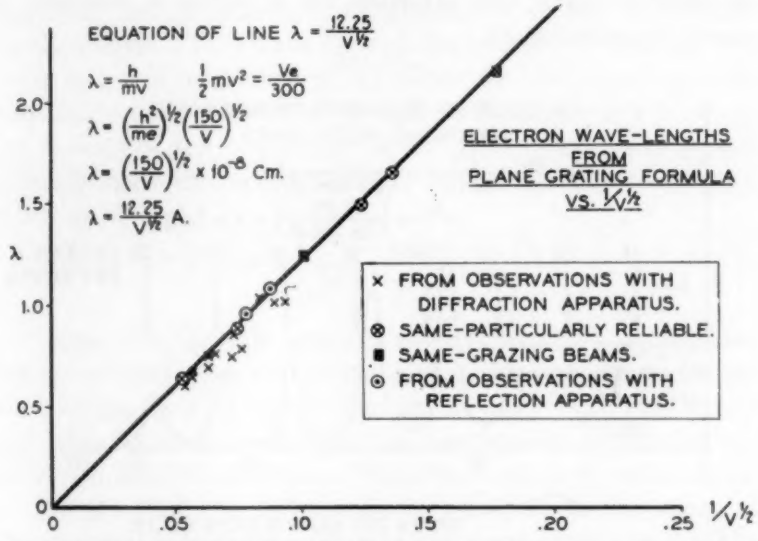
The value of h/mv for electrons that have been accelerated from rest through a potential difference of 54 volts is

$$12.25/(54)^{1/2} = 1.67 \text{ Å.},$$

which is in good agreement with the value 1.65 Å. which we find by our measurements. For "65-volt" electrons the theoretical wave-length is 1.52 Å. and our observed value is 1.50 Å.

We have made in all twenty or more determinations of electron wave-lengths. All of these values are plotted in Fig. 14 against the reciprocal of the square-root of the accel-

FIG. 14.



Graphical comparison of all experimentally determined values of electron wave-lengths with the relation $\lambda = h/mv$.

erating or bombarding potential. The values which we have reason to believe are the most reliable are enclosed in circles or in squares. The straight line through the origin is the graph of the equation

$$\lambda = 12.25/V^{1/2}.$$

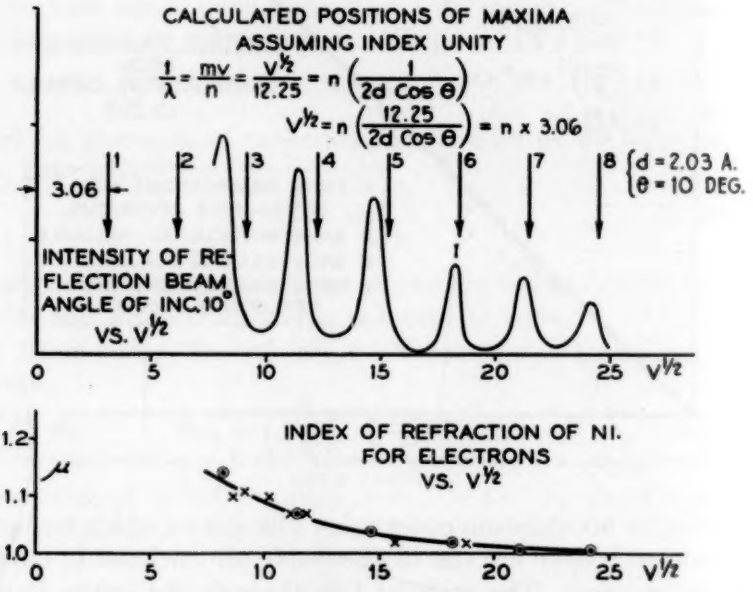
If the experimentally determined wave-lengths agreed exactly with the values of h/mv, all of these points would fall accurately on this line. The departures are none of them greater than can be reasonably accounted for by the uncertainty of the measurements. We may say, I think, that in certain circum-

stances a stream of electrons of speed v behaves as if it were a beam of waves of wave-length h/mv, in accordance with the postulates of the wave mechanics.

And now I would like to return for a few minutes to a further consideration of the regularly reflected beam.

You will remember that we plotted the intensity of the electron reflection beam for angle of incidence ten degrees against the square root of the bombarding potential and obtained a curve characterized by a series of maxima at nearly equal intervals.

FIG. 15.



We can now calculate the positions these maxima would occupy if the index of refraction of nickel for electrons were unity. We have

$$\frac{1}{\lambda} = \frac{mv}{h} = \frac{V^{1/2}}{12.25} = n\frac{1}{2d\cos\theta},$$

that is, we assume the wave-length of the electrons to be $h/mv = 12.25/V^{1/2}$ and apply the Bragg formula to find the

values of $V^{1/2}$ at which the reflected beam should exhibit intensity maxima. Substituting for d and θ their values, 2.03 Å. and 10 deg., we find

$$V^{1/2} = n \times 3.06.$$

If the index were unity, the maxima should be found at these values of $V^{1/2}$. These positions are indicated in Fig. 15.

The observed maxima lie to the left of the calculated positions, the displacement decreasing, however, toward the higher orders. This is the type of displacement to be expected if the index of refraction of the nickel for electrons is greater than unity. We can in fact use these displacements to calculate values of the refractive index. The more general form of the Bragg formula applicable to the case in which the index is not unity is

$$V^{1/2} = n\left(\frac{12.25}{2d(\mu^2 - \sin^2\theta)^{1/2}}\right).$$

Using this formula and the data now available, we have indices of refraction for electrons of various speeds and these are plotted in the lower diagram in Fig. 15. The values indicated by circles are from the observations at ten degrees incidence, and the others are from observations at other angles.

We see that the index approaches unity as the speed of the electrons is increased; that is, the results indicate that the purely geometrical differences between the reflection and diffraction of x-rays on the one hand and of electrons on the other disappear for electrons of high speed. That this is true is evident from the very interesting experiments recently reported by Prof. G. P. Thomson of the University of Aberdeen who has studied the diffraction of beams of high-speed electrons (15,000 to 60,000 volts) by extremely thin metal foils. What Prof. Thomson observes is that electrons of these speeds are diffracted by the polycrystalline metal in the way familiar to us in the powder method of x-ray diffraction devised independently by Hull, and Debye and Scherrer. The cross-section of the transmitted beam consists of a

central spot surrounded by a number of concentric rings. These rings seem to correspond exactly to the rings that would be observed if the incident beam were a beam of x-ray of wave-length equal to h/mv. For electrons of such high speeds the index of refraction of metals is apparently very nearly unity.

Are electrons waves? The easiest way of answering this question is to ask another. *Are x-rays waves?* If x-rays are waves, then so also are electrons. But we are no longer so certain as we used to be that x-rays are waves. The Compton effect and the photoelectric effect are most simply described by supposing that there is some sense in which x-rays are particles.

It is all rather paradoxical and confusing. We must believe not only that there is a certain sense in which rabbits are cats, but that there is also a certain sense in which cats are rabbits.

I would not have you think, however, that confusion in these matters is universal. There are plenty of theoretical physicists to whom these matters are not at all confusing. I am sure that Professor Swann here would not admit to the least confusion. I may cite also Professor C. G. Darwin of the University of Edinburgh. In a recent article on this subject Prof. Darwin writes:

"The central difficulty of the quantum theory has always been the conflict between waves and particles. On the one hand, we have the theorems of conservation of matter, energy, etc.; these tell us that matter keeps together, and endow a particle or a quantity of energy with individuality, so that we can trace its history. On the other hand, we have the theorems of interference—of light and now of matter as well, which as definitely tell us that the things which we before regarded as particles must spread, and so must lose their individuality. The recent work of Bohr explains, at any rate in outline, how the apparent contradiction is to be reconciled. The two lines of thought are not contradictory, but complementary. They do not come into conflict because

they never meet. To verify conservation we must obviously have an enclosed system, and this excludes observation of what happens in the enclosure. If nothing is observable, it is only proper to say that nothing is happening; the system is settled into a spaceless and timeless stationary state outside our intuitions. On the other hand, if we want to observe what happens, we must make a hole in the enclosure and see what leaks out. By the very act conservation is destroyed, but in exchange we get interference phenomena, and these introduce geometry and so a connection with space and time. This very inadequate description shows that we are entitled, when we want to discuss happenings in space and time, to make full use of the wave theory and to pay no attention to the conservation difficulties, because in fact these do not arise."

As you see, it is really all very simple.

The Magnetic Anisotropy of Crystalline Nitrates and Carbonates. K. S. KRISHNAN AND C. V. RAMAN. (*Proc. Roy Soc.*, A 772.) The connection between the crystalline structure of solids and their magnetic properties has recently been accentuated. In this paper the authors discuss the lack of magnetic symmetry in certain nitrates and carbonates that are diamagnetic. "These substances are especially simple because as is well-known from the work of Kossel, Bragg, and others, they consist of charged ions held together by electrostatic forces, so that we can attribute the magnetic anisotropy of the crystal to that of the individual ions. Thus, for instance, in the case of sodium and potassium nitrates we may reasonably look for the explanation of observed magnetic anisotropy of the crystal in the structure of the nitrate ion, since presumably the metallic ions are more or less isotropic." $NaNO_3$ and $CaCO_3$ both belong to the trigonal system. In both the magnetic susceptibility is greater parallel to the trigonal axis than perpendicular to it. For the nitrate the susceptibilities in the two directions are 29.5 and 24.1 $\times -10^6$; and 40.6 and 36.4 $\times -10^6$, for the carbonate KNO_3 and $CaCO_3$ (aragonite) are both rhombic and show the greatest susceptibility parallel to the "c" axis.

Making use of data on magnetic double refraction, on the optical constants of the molecules, and on the depolarization of scattered light the authors calculate the directional difference of the susceptibilities of the two nitrates and find them to agree quite well with the measured values. In the NO_3 group there are three oxygen atoms at the corners of an equilateral triangle, the nitrogen atom being at the center.

It will be recalled that Prof. Raman, F.R.S., attended the centenary of The Franklin Institute in 1924. G. F. S.

THE ENGINEERING OF NAVAL AND COMMERCIAL AIRCRAFT.[1]

BY

EDWARD P. WARNER, M.S.

Assistant Secretary of the Navy for Aëronautics.

THE very title of my address to-night, and the fact that I should have been invited to deliver it before a body primarily interested in scientific rather than industrial problems, is indicative of something exceptional about the aëronautical industry. When we talk of aëronautical engineering we impart to the specific adjective a subtle force which implies that the engineering of aircraft is definitely set apart from any other branch of the profession. We suggest that it possesses, as aëronautical engineering, an individual significance, a degree of separatism, which we do not attach to the engineering of machine tools or automobiles or hydraulic turbines. If we find the reasons for that special position, we approach very near to the heart of the profession's problems.

The sub-division of the engineering profession, which began when the military and the civil engineer recognized that their interests did not run on lines universally parallel, has in general proceeded through the definition of very general classes of employment. To define a professional man as a mechanical engineer is scarcely more specific than to say that he is a doctor and a specialist without declaring the nature of the specialty. Electrical, chemical, and civil engineering are equally broad. Each is rather a term descriptive of a type of training than an identification of a specific employment.

From that rule of generality in sub-division there are only a few exceptions, and they do not exist without reason. I have in mind now a leading engineering school which offers

[1] Presented at the Annual Meeting of the Institute held Wednesday, January 18, 1928.

approximately a dozen distinct professional curricula. Of the number there are but two which are addressed specifically and narrowly to a single industry. Aëronautical engineering and naval architecture are the select pair, and their selection to the eminence of separate treatment is not an exclusive eccentricity of one institution.

If we assume that it is something more than mere chance which leads to the picking out of the aircraft and shipbuilding industries as inviting a special and individualized course of preparation for their technical men, we may search for the motives behind the choice. Very obviously, despite the fact that the engineering of aircraft has been the object of extended special study by professional men for but little more than a decade, while the design of ships in the light both of research and of the empirical application of knowledge gained through experience has been practiced for centuries, there is much in common between the two. Both marine and aëronautical engineering involve the penetration of a fluid as their most fundamental problem. Both depend upon the screw propeller for propulsion through a yielding medium. Both involve serious and similar, although by no means identical, problems of stability and of control. In both cases the reduction of structural weight is a consideration of importance, although of far more trivial significance in the design of a ship than in that of an aircraft. In both instances it is indispensable that adequate strength should be secured, despite the fact that the forces acting can be determined only with extreme difficulty. Structural failures in stationary machinery, or even in terrestrial vehicles, may be productive of danger or they may involve nothing but annoying delay and the expense of repairs, but in a ship or an aircraft, as in a bridge or a building, the results of a collapse of a major element of the structure are almost inevitably catastrophic. Bridges and buildings, it is hardly necessary to remark, are virtually immune from limitations upon weight, but in airplanes, at least, the factor of poundage almost transcends all other considerations in design, and the problem of the engineer is correspondingly complicated and specialized.

Equally noteworthy with the points of kinship between marine and aëronautical engineering in their application to the design of the craft are the similarities in the problems of operation and of navigation upon the surface of the sea and in the air. The mariner and the aviator alike pursue their careers in elements other than the normal abode of earth-dwelling man. Starting with a common understanding of mysteries obscure to the landsman, they find themselves drawn together by sympathetic bonds which go far to explain the facility with which the airplane has been absorbed into the naval organization.

No less striking than points of substantial identity between the work of the naval architect and the airplane designer, however, are those of dissimilarity and contrast. The importance of research upon fundamental principles and of the acquisition in the laboratory of quantitative data antecedent to the making of practical trial upon the finished structure in the field is enhanced in the case of aircraft by the awful sharpness of the line of demarcation between success and failure. It may be doubted if any professed practitioner of the art of ship design since the days of Robert Fulton, given a power plant which was capable of turning itself over, has either built a vessel which would not float or one which was totally unable to move along the surface of the water, but the years that have passed since total failure of a new airplane to leave the ground was quite in the commonplace order of things are but a handful. The margin of performance in present-day aircraft is so large that the specter of inability to rise into the air has ceased to haunt even the most inexperienced designer, but in the early days it was a very easy matter, if preliminary application of the results of research were neglected, to let the overall efficiency of the craft slip below the critical point at which flight became possible.

To that more than to anything else has been due a substantial modification of the relative place of empirical and rational methods in the development of the airplane, as

compared with other mechanical devices. It has been the usual rule, notably exemplified in the history of the automobile, that a beginning is made with mechanical ingenuity and invention immediately incorporated into design, that progress is had for a considerable period by practical trials and by the devising of a series of expedients to remedy the things that go wrong, and that it is not until much later that intensive and systematic research comes upon the scene as the guardian angel over further development.

With the airplane, research has been ever present, from the very beginning and before. The most serious students of the problem before that December day twenty-four years ago when man first flew began their studies not by the construction of an airplane, but by the building of a wind tunnel or a whirling arm where preliminary studies could be patiently conducted. From that winter's day at the beginning of the century when history was made upon the isolated barrier beach of North Carolina down to the present, if the family tree of the finished product upon the flying field be traced, it would be found to have its roots in the laboratory. Aëronautical engineering is directly and explicitly a branch of physical science, perhaps more vividly so than any other phase of engineering work, and it is necessary to approach any analysis of the present status of the aircraft engineering art from a clear understanding of that governing fact. Whatever else a successful airplane may or may not be or do, it must accord with aërodynamic fundamentals, and the magnitude and distribution of the immensely complex reaction of the air upon the structure moving in the fluid must ever be the primary consideration in design.

Not only was laboratory study the stay to which the newly developing art of airplane design clung for support and guidance in the weakling days of its infancy, but it has continued the dominant factor to an extent far larger than is commonly appreciated.

It is a common case that a mechanical art in its evolution pursues a cyclic course oscillating between two more or less

distinct sources of inspiration to progress. The improvement in detail resulting directly from pure research and the mechanical invention which often grows directly out of laboratory study or mathematical analysis, but involves something more as well, alternately claim the principal rôles. Research increases the fertility and productivity of ground already discovered, but it must be supplemented by the inventive faculty to move out into entirely new territory. Research upon frictional forces and their variations could increase the stopping power of the brakes of an automobile and the ease of applying them, but the placing of brakes upon four wheels instead of two involved not merely such studies as those, but also new problems in design, making exacting demands upon the mechanical ingenuity of the designer. The conception of the change presented the obvious possibility of great improvement in braking performance, but opened up, too, the vista of a whole new field of research, and laid upon the student of fundamentals and the laboratory worker a new responsibility which must be met before the theoretical possibilities of the new system could be realized in practice.

That example has been taken as a convenient and a universally familiar one from a non-aëronautical field. It would not be so simple to find one generally known within the recent experience of the aëronautical engineer, for invention, although by no means entirely lacking from the development of the airplane, has been of comparatively secondary importance there for a number of years. In all its fundamentals the heavier-than-air flying craft is today what it was fifteen years ago, the most striking change having been in the elimination of external structural bracing and the use of self-contained wing structures on a considerable number of machines. New structural materials have been introduced, such improvements in detail as the use of brakes and hydraulic shock absorbers have been made, and new methods of construction have appeared, themselves largely the result of research work on stress distribution, secondary

stresses, and metallurgical phenomena. The typical plane, however, has in 1928 an arrangement of wings, a shape of body, and a power plant location, a group of tail surfaces, and a landing gear, all very similar in their superficial and external appearance to those of 1914. It has recently been remarked by a distinguished aëronautical engineer in a certain European country that the training machine which was standard in that country thirteen years ago still bears the aspect of a good up-to-date design, and with a modified power plant is still in regular use, and he suggests that despite the novelty of the aëronautical art and the solicitude with which governments everywhere have fostered its development, a thirteen-year-old airplane is far less obviously obsolete than a thirteen-year-old automobile.

The entire validity of that observation might be open to dispute, but it possesses at least enough truth to be very suggestive, especially when considered in conjunction with a comparison of the relative quality of the performances of the machine in 1914 and of that of the present day. During that period records have been doubled and more than doubled. However slightly it may show itself in the principal externals of appearance, the improvement has been vast, and it has not been due primarily to striking innovations, but to steady progress in matters of detail as a result of patient and systematic study into the physical phenomena upon which design rests. Thirteen years ago, for example, but little was known about the magnitude of the total load on an airplane structure in maneuvers, and still less about its distribution over the surface of wings and tail. What information did exist on that point was the result of speculation and mathematical analysis, rather than of any direct measurement. The structure of an airplane being enormously complex and redundant, a further set of assumptions of uncertain reasonableness had to be made to determine the magnitude of the stresses which would be imposed in individual members by the assumed loads, and when that had been done uncertainty entered from a third point of the compass, for students of

structural theory had not at their command any adequate means of determining the strength of a member of more or less irregular form or of a complex assembly of thin metallic sections intermittently and partially stayed and subjected to a combination of bending, shearing, and compressive or tensile loads.

Eighty per cent. of all of those difficulties have been overcome. Loads have been measured in flight and the mode of their distribution analyzed, and aircraft stress analysis has made enormous strides from the points of view both of determining the loads in the individual members and of calculating the strength which they can be expected to manifest. Structures are lighter and more efficient and are proving more reliable under strains of a severity undreamed of even at the beginning of the present decade, and the progress that has been made in the theory of design is chargeable to the continuous labors and effective coöperation of the mathematician, of the metallurgist, and the research worker conducting free flight tests in conjunction with his studies of aërodynamic principles in a laboratory.

The dependence upon research has been universal and every successful design shows its influence, but the designer has sometimes made contact with the research establishment only at second or third hand, and has absorbed the results without fully realizing whence they came. It is a distinct need of the hour that that should cease to be so, and that the engineer and the research worker should be brought into closer liaison. However well qualified an aëronautical engineer may be in the making of stress analysis according to a standardized system, he is not fully competent unless he has a clear understanding of the processes whereby the load factors and allowable stresses given him in a specification were arrived at and of the nature of the free flight and laboratory experiments employed in their derivation.

The obligation is bi-lateral. Neither designer nor experimenter can do his work effectively if he isolates himself in a compartment proof against sound or sign of what is going on

in the outside world. The student of research ought to be familiar with the air from personal experience and to have a personal and direct acquaintance with the practical necessities that confront the designer or constructor of airplanes. Often in the past the two have been far apart, without recognition of the reality of their mutual dependence. It is the responsibility alike of those now engaged in aëronautical work on their own account and of teachers preparing the engineers and experimenters of the future to see that no such state of affairs shall henceforth exist, either in the largest industrial unit or in the smallest. Liaison is best assured when the industry is doing some research work on its own account, and the fact that the field has been one of great government interest is no adequate excuse for failure on the part of an airplane manufacturer to carry on his own experiments and to gain within his own organization some information which will ultimately become a contribution to the general stock of knowledge of the fundamental science. There are noteworthy examples even now of the direct participation of the aircraft industry in research. They should be multiplied.

One may well feel some diffidence about assuming the rôle of the prophet in anything relating to aviation, but I believe myself quite within bounds of safety in expressing confidence that systematic research will continue as important in the future as in the past. Furthermore, I am confident that its importance will be, as it deserves to be, more and more fully recognized. It would not do to ignore or deny the possibility of invention producing a fundamental modification in the whole mode of operation of heavier-than-air craft, but whatever happens, the laws of aërodynamics will remain unchanged and will continue to govern the behavior of every machine that flies, however the details of its means of propulsion and of support might be changed. Anything may happen, but for myself I am not among those sanguine spirits who expect to see the airplane as we now know it displaced by some radically different machine capable of vertical ascent or descent, or other valuable novelties of performance. Such devices deserve the most serious con-

sideration and examination and they may well prove of great usefulness in certain employments, but they are subject to fundamental difficulty in that they all involve some continuously moving parts within the structure. A rigid structure can be designed so that its chance of collapse is infinitesimal, but as soon as bearings and moving parts are introduced, even with the most careful design and the most watchful maintenance, there exists the chance for something to go wrong. If upkeep is as slack as it is likely to become in the hands of the average private owner, that chance is magnified. It is precisely because they necessitate continued operation of a number of working members that airplane engines sometimes fail, and if the aërodynamic elements of the craft involve moving blades and bearings and pivoted connecting links, the possibility of failure is no longer limited to the power plant. The great beauty of the existing type of airplane is that its minimum condition of safety is merely that a rigid structure shall hold together and that three sets of control surfaces shall continue to swing freely on hinges as simple as those of a door. Given those conditions, the engine can stop, or any part of its structure can break, and the shaft can seize. It can even blow up entirely and part of it fall to the ground, and yet the pilot can make a safe descent. To complicate the structure is to make the minimum conditions of safety less simple and sure, and it is because most of the proposals for radical modification in the fundamental method of operation of heavier-than-air craft are suggestions for increasing complication and for introducing new working parts that I view them as a whole with a considerable skepticism.

All airplanes are subject to the same general laws. Performance is calculated for all in the same fashion, and all machines in practical service at the present time depend upon the same means of control, yet those points of universal similarity do not imply a standardization of practice in design. The evolution of the airplane has been via research programs of which most of the elements applied in some degree to the design of every conceivable type of machine,

but it has been an evolution of constantly increasing functional specialization in design and increasing differentiation of types with difference of intended purpose.

The quest for a universally applicable formula, for a hard and concrete statement of what is "best" in design, has been persistent and unavailing. One of the many committees which investigated the aëronautical activities of the government of the United States made a special effort to secure some sort of a "yardstick" whereby statesmen comparatively uninstructed in the purely technical aspects of aviation could rate the merits of aircraft, but the effort was, and would be likely always to be, in vain. What is best depends upon the end to be accomplished. Neither monoplane nor biplane has proven itself definitely and generally superior to the other. Machines with external bracing have neither driven from the field, nor been overcome by, those with the structure contained within the wings. Airplanes with one engine and those with two engines and those with more exist side by side. The problem of aëronautical engineering is the adaptation of complex physical phenomena in such a way as to extract from them the maximum of advantage under a given set of circumstances, while at the same time remaining within the bounds of certain definitely imposed mechanical limitations. Both the circumstances and the limitations are defined by the nature of the work which the aircraft is to do.

The problem is essentially one of analysis and classification of the requirements to be met. In commercial aviation, silence, ample cargo space within the body of the craft, and passenger comfort impose their restrictions upon the will to follow to their ultimate degree the suggestions of aërodynamic and structural theory. In naval operation and so in the engineering of naval aircraft the special sources of perplexity ever present are the need for seaworthiness and the limitation on space.

If airplanes are to be of the broadest utility in naval affairs, they must travel on shipboard, for those aërodynamic

laws before which obeisance has already been made as the arbiters of our destinies impose inexorable limitations upon the range and the period of endurance of mechanical flight. Airplanes have crossed oceans, but to be able to go out and make the same flight in any weather and carrying a military or commercial load is quite a different matter, and there is not, nor is there any prospect that there soon will be, capacity in any heavier-than-air craft to accompany a fleet and be able to participate in all naval operations while remaining continuously on the wing. The base from which flight is started and at which it terminates must be either on shipboard or on the surface of the water. The airplane must go to the ship, and not only does the deck of a vessel offer a grievously restricted landing field, but every cubic foot of storage space in the hold is jealously prized. The aëronautical engineer applying himself to naval problems has to produce airplanes fitted for every type of service that they may be called upon to render in the military organization on shore, approximating as closely as possible to the best characteristics of performance that could be attained if operation were free from any special restriction. They must, however, at the same time provide in performance characteristics and in structure for the ability to be projected into the air and to be landed again within the confines of the deck, and the overall dimensions must be kept exceedingly compact so as to render possible the storage of a maximum number of airplanes within the cramped confines of a hangar deck on a ship. Aëronautical engineering practices in the Navy and in commerce have diverged enough by reason of the peculiarities heretofore mentioned to cause the production of specialized machines of strikingly dissimilar appearance. They remain fundamentally one and the same, dependent on the same principles and the same researches. They may best be practiced, with both technical and industrial profit, within the same organization, the members of which have proceeded from a firm grasp on sound first principles to a secondary, although no less important, study of the separate and somewhat variant experiences and needs of the multitudinous types of aërial operations now practiced.

Manufacturers Recommend Tolerances for Certain Medicinal Tablets. The Contact Committees of the American Drug Manufacturers Association and the American Pharmaceutical Manufacturers Association have submitted to the Food, Drug and Insecticide Administration, United States Department of Agriculture, their fourth report containing recommendations for tolerances on certain medicinal tablets. They have indicated the degree of accuracy within which properly manufactured medicinal tablets can be made under present-day manufacturing methods.

This report covers recommendations on eleven compressed tablets and includes recommended methods of analysis. The tolerances suggested by the combined Contact Committees for the compressed tablets mentioned are as follows:

Acetphenetidin	7½ per cent.
Acetylsalicylic Acid	7½ " "
Ammonium Chloride	6 " "
Hexamethylenetetramin	6 " "
Potassium Chlorate	6 " "
Potassium Iodide	6 " "
Potassium Permanganate	6 " "
Quinine Sulphate	9 " "
Sodium Bicarbonate	7½ " "
Sodium Salicylate	9 " "

The proposed standard for Chloramin-T tablets is that they shall contain active chlorine corresponding to 10.3 per cent. to 14.3 per cent. of the labeled amount of Chloramin-T.

INSTRUCTION ON THE MAKING OF POTASSIUM-HYDRIDE PHOTOELECTRIC CELLS.

BY

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Bartol Research Fellow.

BARTOL RESEARCH FOUNDATION
Communication No. 23.

The photoelectric cell is fast becoming an indispensable unit in the modern laboratory, and, although there are some cells to be had on the commercial market, they may not always satisfy the particular physical or electrical requirements of special applications. In answer to just such a need, this laboratory has developed a method by which photoelectric cells of high sensitivity can be made. There is, we think, nothing unique in the method and there may be other ways which we have not thought of which are better. All that we claim for the following instruction is that it describes in detail a procedure by which photoelectric cells can be easily produced in the laboratory with a fairly high degree of certainty that the cells will turn out successfully and be reasonably uniform in their sensitivity.

In the most general terms, the method usually followed in the production of this type of photoelectric cell is as follows:

(1) The cell is designed and constructed carrying two electrodes, the "outside" electrode connecting to the light-sensitive surface, and the "central" electrode, which is the collector of the electrons.

(2) The tube is connected to a suitable vacuum system, evacuated, and baked out at high temperature.

(3) The potassium is distilled in "vacuum" through part of the system and condensed on the surface of the cell.

(4) Hydrogen is then introduced to suitable pressure and a glow discharge is operated between the "outside" and the "central" electrodes until the potassium-hydride surface so produced shows the maximum sensitivity.

(5) The hydrogen is then pumped out and argon is introduced to give maximum sensitivity.

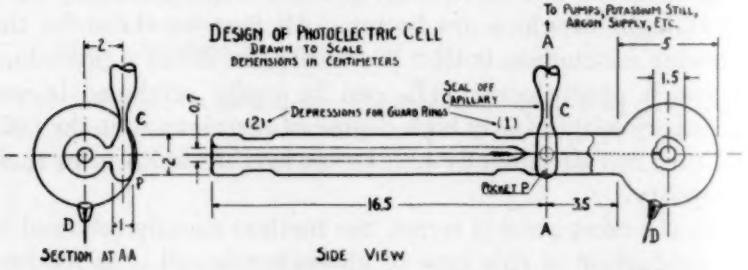
(6) The cell is then sealed off and is ready for use. All of this can be found in the literature.[1] The intention of the following instruction is simply to show one method by which these generalities can be reduced to the specific case for the benefit of those who are not specifically interested in the study of photoelectric cells as such, but are interested in using them as a laboratory instrument.

PREPARATION.

1. *Photoelectric Cell.*

The design of the cell depends on the type of work in which it is to be used, and therefore the specifications given here are to be taken simply as an example embodying many of the requirements common to all cells. The dimensions in cm. are given in the sketch in Fig. 1.

FIG. 1.



Features of the design shown here which might escape one's notice are called to attention in the following, and the reasons for their incorporation are given.

The cell should be made of Pyrex glass because it will withstand more heating in the presence of potassium without becoming brittle than other kinds. The connection (*A*) with the vacuum system and potassium still, should be made on the neck of the tube because in the distillation process it is necessary to keep the bulb cool. The "pocket" (*P*) at the entrance to the cell is provided in order to catch the liquid

[1] H. E. Ives, *Bell System Technical Journal*, 5, 320–335 (1926).

potassium after it passes through the capillary (*C*). The metal is heated in this pocket and passed into the cell as a vapor. If liquid metal is run directly into the hot cell, there will be the danger that it will break the glass due to the sudden chilling. If the potassium vapor instead of the liquid metal is run through the capillary, the distillation process will be found to be unnecessarily difficult as well as tedious. The space of 3.5 cm. between the pocket and the bulb is provided in order to make room for the air cooler to keep the bulb cool and to give space for the asbestos shields placed there to protect the bulb from the flames used in the distillation. See Fig. 6.

During the distillation, this part of the tube is kept at a temperature of about 300° C. by an electric heater which must be wound on before the cell is fastened to the vacuum system. The exact specifications of this heater are given below.

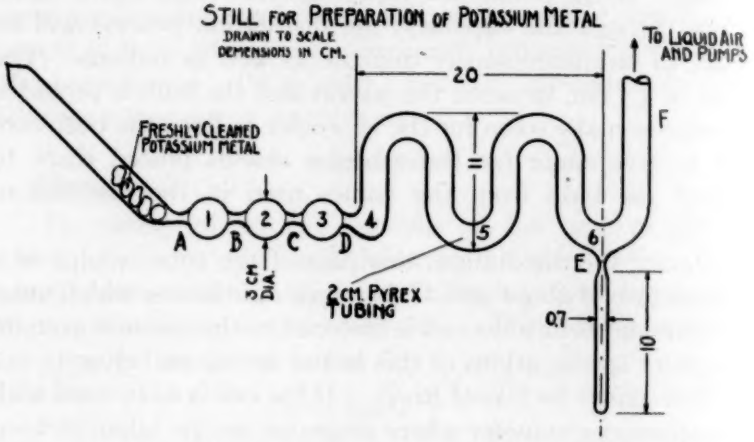
Depressions for Guard Rings.—If the cell is to be used with a sensitive electrometer where steps can not be taken to keep the cell in a very dry atmosphere, guard rings will be found necessary. Fifty to one hundred turns of No. 30 bare copper wire wound in the depressions (1) and (2), shown in Fig. 1, reduce the leakage current to a satisfactory value. The guard ring at (1) will usually be found sufficient if it is connected to "earth" along with the positive side of the battery and the shield of the electrometer. In case there is an electrometer deflection due to the potential of the voltaic cell set up between the copper ring and the tungsten seal of the central electrode over the surface of the glass, this can be greatly reduced by winding a second copper ring in depression (2) and connecting this one to the central electrode. The best way to support the cell when it is in use is by means of a band fitted around the guard ring at (1).

Location of the Outside Electrode.—The outside electrode (*D*) should be placed so that it is at the bottom of the cell when it is mounted on the system. The excess potassium will then flow around the nickel ring fastened to the tungsten seal and thus insure perfect contact between this lead and the potassium coat.

2. *Preparation of the Potassium Metal.*

A type of still in which the metal can be satisfactorily prepared is shown in Fig. 2. Two balls of potassium (1.5 cm.

FIG. 2.

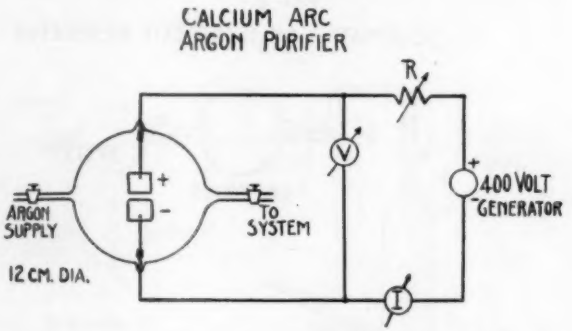


dia.) should be scraped clean, cut, washed in petroleum-ether or carbon-tetrachloride and carefully put into the tube as shown. (*Caution should be exercised not to allow the balls to make a hard impact with each other or with the glass because clean potassium catches fire very easily.*) The tube should be sealed as quickly as possible and the vacuum pump started. After ½ hour of pumping, the parts from "*A*" on through to "*F*" should be baked out quite thoroughly with gas burners. Then melt the potassium slowly into the first sphere (1) and seal off at "*A*." Then distill the metal into (2) and seal off at "*B*," etc. When the metal reaches (4) and "*D*" is sealed, it should exhibit a very clean appearance. Parts (5), (6) and the side tube should again be baked out with the flame. The metal can now be distilled into (5) and then into (6) where it can then be forced to flow down the side tube and sealed off at the capillary *E*.

3. *Purification of the Argon.*

A calcium arc [2] purifier should be connected to the vacuum system through suitable stopcocks as shown in Fig. 5. The calcium arc argon purifier consists of two calcium blocks supported on connections and separated a distance of about 8 to 10 mm. Suitable electrical connections are shown in Fig. 3. The arc can be started after the circuit has been

FIG. 3.



completed by causing the spark from a spark coil or from a Halliwell-Shelton violet ray generator to cross the gap between the electrodes. It is necessary to touch only one of the electrodes with the spark coil connection because the capacity to earth of the battery is sufficient to make the complete circuit for the spark discharge well enough to start the calcium arc. After the arc is started the pressure can be increased from the starting value of one mm. or so to any desired value without danger of putting out the arc. A high driving voltage (400 volts) and a high series resistance (450 ohms) are desirable for a strong and stable arc discharge. With a current of about 0.7 amp. the voltage across the arc should be about 80 volts. Six to eight hours running should "clean up" the argon. Mount the electrodes in the vertical position. A low pressure discharge tube (*G*) should be connected to the system as shown in Fig. 5, so that the argon can be introduced,

[2] The "Misch Metal" arc is thought to be superior to the calcium arc by some experimenters.

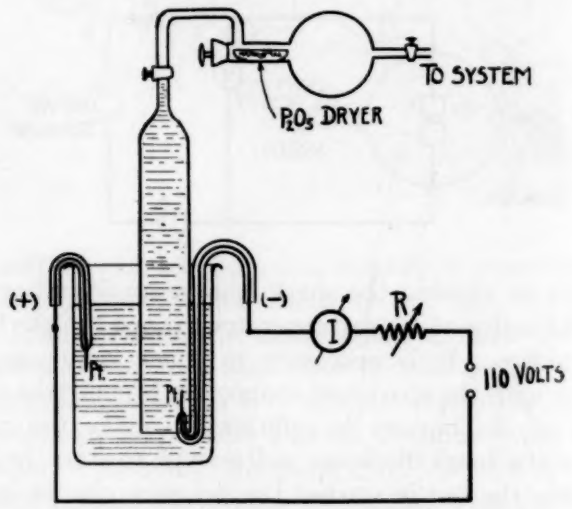
a discharge started, and impurities such as nitrogen be detected by direct vision spectroscopic observation.

4. *Production of the Hydrogen.*

Electrolytic hydrogen [3] produced as shown in Fig. 4 has been found to be suitable for the forming of the hydride. Three liters of freshly boiled distilled water to which has been added 50 gm. of phosphorous pentoxide makes a satisfactory

FIG. 4.

SCHEMATIC OF HYDROGEN GENERATOR



electrolyte. With a suitable resistance R the current can be taken from a 110-volt source and adjusted to 0.5 amp. There is some danger of a little oxygen being carried into the hydrogen side if the generation is too rapid.

HEATERS FOR BAKING OUT AND DISTILLATION.

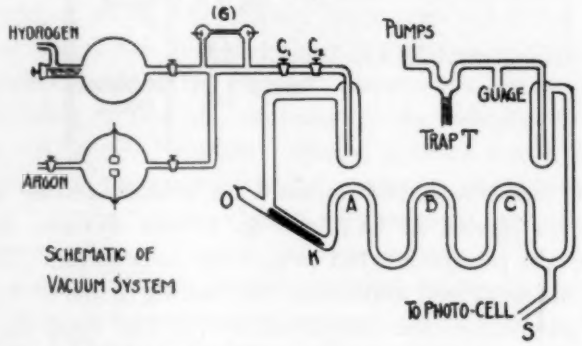
1. *Heater on Neck of Photo-cell.*

Before the cell is connected to the system two electric heating coils should be wound on the neck of the cell as shown

[3] Commercial hydrogen introduced through a palladium valve has been tried in other laboratories and thought to be superior to electrolytic hydrogen.

by H_1 and H_2 in Fig. 6. To make these heaters, wind on three layers of wet asbestos tape. Then wind two meters of No. 20 B. & S. nichrome wire held at each end by two turns of No. 18 copper wire. Three leads should be brought out, one for each end and one at the mid point. Three layers of asbestos tape (width 1.0 in.; thickness 0.015 in.), again wound on wet, will serve as an insulation to protect the outside of the heater. A heating current of 4.0 amps. for each coil can be furnished from a 12-volt battery and adjusted by means of a series resistance in each circuit.

FIG. 5.



2. *Large Baking-out Oven.*

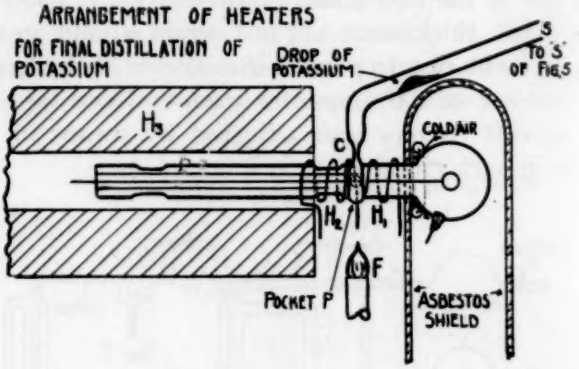
The connection *C–S* (shown in Fig. 6) to the vacuum system must be made to permit the enclosing of the entire cell in an oven in order to bake it out. A baking-out oven 17 inches long and 10 inches in diameter has been found to be perfectly satisfactory for this purpose. A temperature of 420° C. ± 10° should be maintained for a period of at least three hours, after which a temperature of about 340° C. should be held for at least one hour.

3. *Heater to Keep the Neck of the Photo-cell Clear.*

In order to prevent the condensation of potassium in the neck of the cell during the distillation process, a small oven (H_3) of Fig. 6 must be maintained at a temperature of 340° C. ± 10°. Temperature in excess of this value may drive out impurities from the glass which might contaminate the

potassium surface while a lower temperature might allow enough potassium to condense in the neck to give an objectionable "dark current." The capsule of potassium pre-

FIG. 6.



pared as described above should be broken at one end and inserted as shown at (*K*) in Fig. 5; the system sealed at (*O*), and the pumps started as quickly as possible. After the baking out described above and the baking of parts *A*, *B*, etc., with a gas flame, the preparations for the final distillation should be made. The heater (H_3) and the two auxiliary electric heaters should be started and allowed to come up to equilibrium temperature as specified above. Also the air blast coolers should be placed in position so as to keep the bulb cool at all times. (The air blast coolers consist of two perforated glass "half moons" formed so as to fit closely around the neck of the tube as shown.)

Melt the potassium and distill some of it over "*A*," "*B*" and "*C*," and force one drop at a time to roll down the side tube to the cell through the capillary and into the pocket *P*. One drop will fill the pocket if made the size shown in Fig. 1. The bunsen burner (*F*) shown in Fig. 6 should be adjusted to keep the pocket warm but not hot enough to cause rapid distillation. As soon as the drop has been driven into the pocket, additional heat from a small "gas-air" flame of a hand torch will quickly vaporize the metal, drive it through the

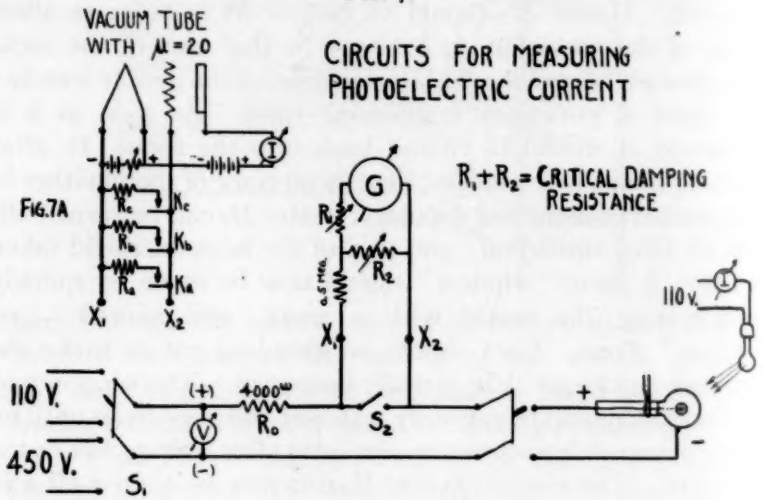
opening in the neck where the electric heaters will keep it vaporized until it has condensed on the wall of the cool bulb. After three drops have been introduced in this way, the metal left in "*A*," "*B*" and "*C*" should be heated just enough to coat the inside of these tubes completely. This coat will help remove any impurities contained in either the argon or the hydrogen, which might otherwise contaminate the surface of the cell. Heater H_1 should be tu ed off in order to allow some of the potassium to condense i that part of the neck. The bunsen burner should be remove and the pocket watched for signs of potassium condensing there. As soon as it is observed, it should be chased back into the tube. If, after waiting about five minutes, there is no trace of metal either in the pocket or along the capillary, heater H_2 can be turned off; the air blast turned off; and part of the asbestos shield taken away. A small "window" should now be made by quickly evaporating the metal with a small, well-pointed "gas-oxygen" flame. Care should be exercised not to make the window any larger than is really necessary. The window and the pocket should be carefully watched and kept clean until no trace of metal deposit can be seen even after waiting five or ten minutes. The electric heater H_3 can now be turned off and removed.

CIRCUITS FOR MEASURING PHOTOELECTRIC CURRENT.

Two circuits for measuring the photoelectric current are shown in Fig. 7. The direct measurement method shown in the figure requires the use of a sensitive galvanometer such as the Leeds-Northrup 600-ohm instrument with a sensitivity of 13,000 megs. With this circuit it is easier to obtain quantitative results than with the circuit 7*a*. Circuit 7*a*, which can be inserted in Fig. 7 at x_1–x_2, has the following definite advantages: (1) Response is almost instantaneous; (2) during the time that the gas is being introduced into the cell continuous measurements of the photoelectric sensitivity can be made without the danger of overloading the measuring instrument in case a glow unexpectedly starts within the cell. The circuit shown in Fig. 7*a* should be set up with the vacuum

tube (with $\mu = 20$ to 30), the resistances (R_a, R_b and R_c) and the keys (K_a, K_b and K_c) in a tight box with a dryer such as phosphorous pentoxide. Resistances R_a, R_b, R_c, etc., should be made in the usual way by drawing a long heavy line [4] with india ink in the form of a grid to give approximately the following resistances: $R_a = 300$ megs; $R_b = 40$ megs; $R_c = 6$

FIG. 7.



megs and $R_d = 1.0$ meg. If these resistances are mounted in glass tubes with connecting electrodes and evacuated, they will be found to be very free from "galvanic e.m.f.," and polarization, and remain constant indefinitely. The keys (K) should be designed after the manner of electrometer keys and be operated by strings as in the usual electrometer set up. With K_a operated and no current flowing through the cell, the grid of the tube will be at the potential of the negative side of the filament.[5] When a current flows through the cell and the resistance R_a, the grid becomes negative with respect

[4] A line 1.0 mm. wide has a resistance of approximately 1.0 meg per cm. and one 0.4 mm. wide has a resistance of about 3 megs per cm. For most applications the mounting of the resistances in vacuum is not necessary.

[5] If the filament is not burned too brightly, the filament to grid current flowing through the 300-meg resistance will be less than $2(10)^{-9}$ and will introduce a small error only while the photoelectric current is small.

to the filament by the amount $V = R_a i$ and the plate current I of the tube will *decrease*. From the "grid voltage, plate current" characteristic of the tube, the V corresponding to the observed value of I will be known. Curves can be plotted (one for each value of R), which relate the plate current I and the photoelectric current i and thus make measurements with this circuit almost as quantitative as the more direct galvanometer method. The advantages of this method of measurement from the standpoint of safety and speed are obvious. In case a glow discharge or a short circuit takes place in the photo-cell or in its circuit connection, the current I drops to zero and no harm is done.

FORMATION OF THE HYDRIDE.

One of the measuring circuits drawn in schematic in Fig. 7 should be set up to measure the photoelectric sensitivity using a 75-watt lamp (equivalent to about 100 c.p.) as a source of light at a distance of one meter. With an applied voltage [6] of 110 v. the current should be about 5×10^{-9} amp. The system should be cut off from the pumps by means of a mercury trap T of Fig. 5, and hydrogen introduced by means of the double stopcock trap C_1 and C_2 of Fig. 5, while the photoelectric current is being watched continuously. At a pressure of about 0.1 mm. of Hg. the maximum sensitivity will be reached. The current should now be in the neighborhood of 25×10^{-9} amp. After the galvanometer has been short-circuited by switch S_2 of Fig. 7, the application of 450 volts at S_1 should start a glow discharge or "flash" within the cell. Cut off the discharge after it has run 0.2 to 0.3 sec. and again measure the sensitivity. It should show a large increase. In case the discharge does not start spontaneously, it can be started with the spark coil. After six to ten flashes of this kind a maximum in sensitivity should be reached with a current of about 400×10^{-9} amp. The system must now be pumped out and "flushed" with argon four or five times and then pumped down for one-half hour or more. Under the

[6] If circuit 7*a* is used, a voltage nearer the critical voltage can be safely used. If one of the electrical restrictions placed on the problem is the operating voltage, then that required voltage should be used here instead of 110 volts.

vacuum condition the photoelectric current should be 80 $\times 10^{-9}$ amp. The introduction of argon to a pressure of about 0.1 mm. should bring the cell up to its maximum of sensitivity with a current of about 600 $\times 10^{-9}$ amp.

DETERMINATION OF THE CRITICAL VOLTAGE.

With the galvanometer well protected by shunt and series resistances (R_1 and R_2), gradually increase the voltage until a rather sudden increase in current shows up which does not depend on the presence of the light source. Cut off the potential and again bring it up slowly to within about 10 volts of the critical voltage just found and make sure that the current falls to zero when the light is out. The current flowing with this voltage (180 − 10 = 170 volts for the cell described here) should now be about 3500 $\times 10^{-9}$ amp. Seal off the cell heating the capillary at C as quickly as possible and check the reading, supporting it in about the same position as before. Again check this final reading after 48 hours. If no change can be detected within that time this cell can be considered satisfactory and if not misused will remain quite constant in its response for a long time.

TABLE OF PHOTO-CURRENT AT EACH STEP.

Vacuum	5 $\times 10^{-9}$ amp.
Hydrogen to max.	25
Flash to max.	400
Vacuum	80
Argon to max.	600
Critical voltage—10 v.	3500

To Dr. W. F. G. Swann, under whose direction this work was carried out, I am indebted for many valuable suggestions.

DIELECTRIC CONSTANT OF AQUEOUS SOLUTIONS OF SODIUM CHLORIDE.

BY

ARTHUR BRAMLEY

Bartol Research Fellow.

BARTOL RESEARCH FOUNDATION
Communication No. 24.

ACCORDING to the theory of aqueous solutions of strong electrolytes formulated by Debye and Hückel, the dielectric constant D of a solution of concentration y mols. per liter should be expressible in the form

$$D = Do(1 - \alpha y),$$

where Do is the dielectric constant of the solvent,

$$= 81.0 \text{ for pure water,}$$

and α is a constant depending on the types of ions present in the solution,

$$= 6.6 \text{ for NaCl.}$$

Measurements of α have been made by various investigators using a high frequency bridge method, of which those by Sach (*Phys. Zeit.*, 5, 28) are among the best. He finds the value

$$\alpha = 7.1 \pm 1.2,$$

which is in good agrement with the theory, considering the difficulties involved in measuring the capacity of a cell whose conductivity is appreciable. In order to avoid the ambiguity arising from this cause, the writer used, to determine the dielectric constant, an interferometer method, which depends upon the measurement of electrostriction produced in the solution by the applied electric field.

From a study of the dielectric constant of the solution for concentrations up to 4×10^{-2} mol./l., it was found that the

following equation expressed the experimental results to the accuracy of the density determinations,

$$D^2 = D^2o(1 - \alpha^1 y),$$

where

$$\alpha^1 = 15.7 \pm .6,$$

which may be expressed in the following form for infinitely dilute solutions:

$$D = Do(1 - \alpha y),$$
$$\alpha = 7.85 \pm .30,$$

whereas the value demanded by the theory was

$$\alpha = 6.6 \text{ for the same salt, NaCl.}$$

DESCRIPTION OF APPARATUS.

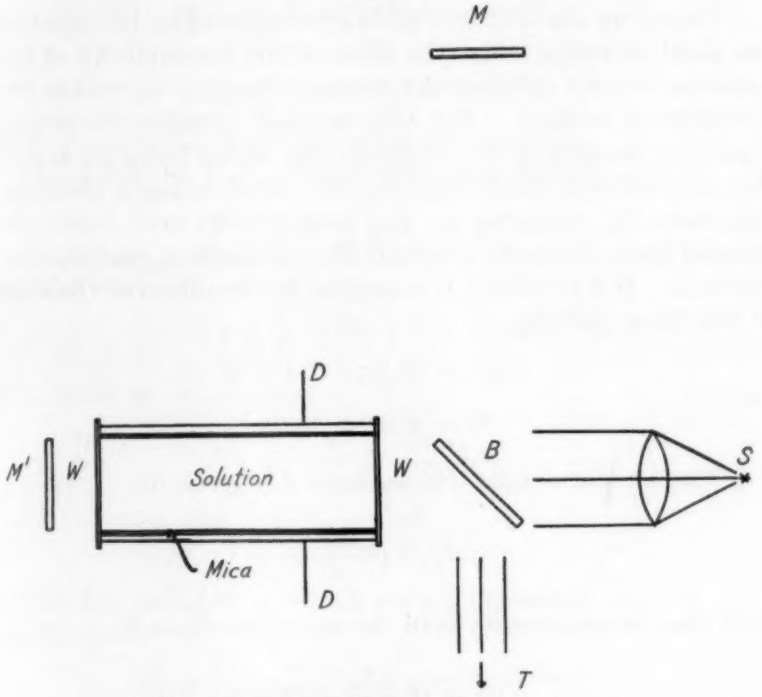
According to the theory of the electrostriction effect as developed by G. Bruhat and M. Pauthenier (*Journ. de Phys.*, Jan. 1925), the adiabatic change in the index of refraction, n, of a dielectric, due to the application of an electric field of intensity E, is related to the dielectric constant D, the index of refraction n, and the coefficient of adiabatic compression X by the relation

$$\Delta n = \frac{(D - 1)(D + 2)(n^1 - 1)(n^2 + 2)XE^2}{144n}.$$

In order to measure the small quantity Δn predicted by this equation, the condenser cell containing the electrolytic solution was placed in one arm of a Michelson interferometer. The fringe system by which the variation of the index of refraction was measured was observed through a telescope by setting the cross-hairs of the instrument on one of the fringes of the system, the readings being accurate to one-twentieth fringe. As a source of illumination, a mercury arc was used from the spectrum of which the green line 5461 Å. was selected by means of a Wratten ray filter as a convenient source of monochromatic light. The cell consisted of a parallel plate condenser 10 cm. long, made of bakelite with two optical glass plates on the ends, the light passing through

the cell parallel to the plates so that the effect could be measured at various positions relative to the condenser plates. The metal plates were insulated from the liquid by thin sheets of mica in order to prevent the disturbances in the liquid pro-

FIG. 1.



D, the electrical connections to metal plates.
M and *M'*, full silvered mirrors.
B, half silvered mirror.
S, light source.
T, telescope through which the fringe system is observed.
W, glass end plates.

duced by the action of minute bubbles on the surface of the plates which separated from them and diffused across the field of view.

As this method consists in measuring the change in the index of refraction of the solution with respect to a certain line when the electric field is applied, the relation between the relative fringe shift f and the change in refractive index Δn must be known; this relation is expressed in the following

equation,

$$\Delta n = \frac{\lambda f}{2l},$$

where λ is the wave-length in air of the light used to form the fringe system and l is the length of the cell.

Before we discuss the type of results found by this method we shall investigate first the effect of the conductivity of the solution on the value of the electric intensity E, within the conducting medium. For this we shall consider the simple case of a parallel plate condenser, the plates being separated by two different dielectrics; the first medium has a dielectric constant D_1, thickness d_1, and conductivity zero, while the second has a dielectric constant D_2, thickness d_2, and conductivity c. If a potential V is applied to the plates at the time $t = 0$, then initially:

$$D_1E_1 = D_2E_2, \qquad t = 0,$$

where

$$V = E_1d_1 + E_2d_2.$$

The current density i in medium I is given by

$$i_1 = D_1\frac{\partial E_1}{\partial t},$$

and the current density i_2 in the second medium is

$$i_2 = D_2\frac{\partial E_2}{\partial t} + cE_2,$$

and from the equation of continuity of current flow we have that

$$D_1\frac{\partial E_1}{\partial t} = D_2\frac{\partial E_2}{\partial t} + cE_2.$$

From the time differentiation of the equality

$$V = E_1d_1 + E_2d_2,$$

we find that

$$\left(D_1 + D_2\frac{d_1}{d_2}\right)\frac{\partial E_2}{\partial t} + c\frac{d_1}{d_2}E_2 = 0,$$

and also that

$$\left(D_1 + D_2\frac{d_1}{d_2}\right)\frac{\partial E_1}{\partial t} + c\frac{d_1}{d_2}E_1 = c\frac{V}{d_2},$$

whose solution is

$$E_1 = \frac{V}{d_1} + E_{10}e^{-[cd_1t/(D_1d_2+D_2d_1)]}$$

and

$$E_2 = E_{20}e^{-[cd_1t/(D_1d_2+D_2d_1)]},$$

where E_{10} and E_{20} are constants of integration.

Since $D_1E_1 = D_2E_2$ when $t = 0$, we have that

$$\left(\frac{V}{d_1} + E_{10}\right)D_1 = D_2E_{20},$$

and also that

$$V = \left(\frac{V}{d_1} + E_{10}\right)d_1 + E_{20}d_2,$$

from which we obtain that

$$E_{10} = -\frac{V}{d_1}\frac{D_1d_2}{D_1d_2 + D_2d_1},$$

$$E_{20} = \frac{V}{d_2}\frac{D_1d_2}{D_1d_2 + D_2d_1},$$

so that the quantity in which we are interested, namely E_2, has the value

$$E_2 = \frac{V}{d_2}\frac{D_1d_2}{D_1d_2 + D_2d_1}e^{-[cd_1t/(D_1d_2+D_2d_1)]}.$$

The values of these quantities for the condenser used in the experiment were

$$D_1 = 6, \qquad D_2 > 50, \qquad \text{while} \qquad D_2 = 81.0 \text{ for water},$$

$$d_1 = 5 \times 10^{-3} \text{ cm.}, \qquad d_2 = 1.8 \text{ cm.},$$

$$c < 10^{-2}/\text{ohms},$$

and V varied from 3,000 to 6,000 volts, so that

$$\frac{D_1d_2}{D_1d_2 + D_2d_1} = 1 \text{ app.}$$

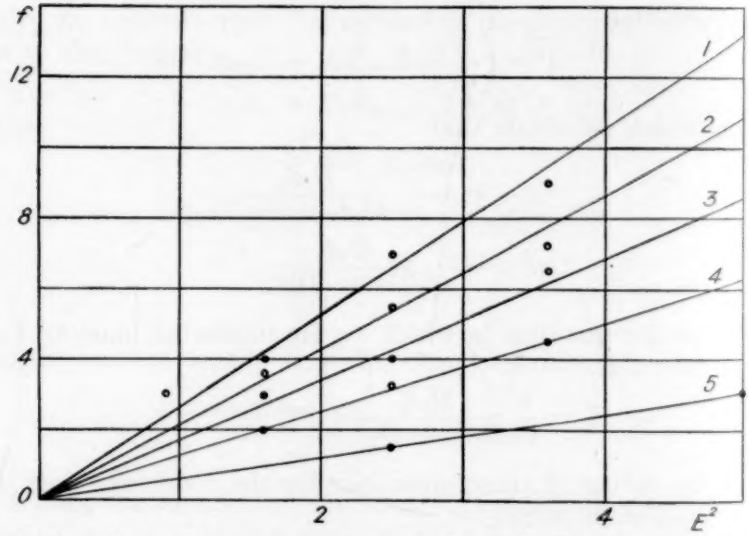
and

$$E_2 = \frac{V}{d_2} e^{-(cd_1t/D_1d_2)}$$

$$= \frac{V}{1.8} e^{-4\times 10^{-4}t},$$

when $c = 10^{-2}$, so that during the period of the alternating electromotive force used as the source of power the variation of the electric intensity due to the conductivity was negligible, a result which was experimentally verified. For knowing the electric intensity within the cell it is easy to calculate the capacity of the arrangement and its variation with time.

FIG. 2.



In this figure, the abscissa represents the square of the electric field, $E^2 \times 10^{-7}$, and the ordinate the fringe shift $f \times 18$. The lines marked 1, 2, 3, ··· represent the values of the fringe shifts against E^2 for

1, pure water,
2, solution, NaCl, concentration $y = .71 \times 10^{-2}$ normal,
3, solution, NaCl, concentration $y = 1.42 \times 10^{-2}$ normal,
4, solution, NaCl, concentration $y = 2.13 \times 10^{-2}$ normal,
and 5, ethyl alcohol.

For the case of water such an experiment was performed by Cohen and Arons who determined the dielectric constant of water by measuring the rate of decay of the charge on a condenser of this type. Since their determination is in good

agreement with those determined by other methods, the values we have found for the electric intensity can be regarded as representing the actual distribution of intensity.

In the experiments which we are going to describe, the variation of the refractive index for a solution of fixed concentration was determined experimentally for the potential differences V on the plates ranging from 3,000 to 7,000 volts. In all the solutions investigated the variation of the index of refraction Δn varied as V^2 within the limit of observation of the fringe shift, an effect we should expect, for from equation I we have that $\Delta n \propto E^2$, while from the theory of the distribution of electric intensity within the cell we have that

$$E \propto V.$$

The data obtained are given in Fig. 2, where we have plotted the fringe shift f in units of 1/18 of a unit fringe shift against the square of the applied field V. The results show that for water and solutions of NaCl in water at three different concentrations the observed points lie on a straight line in each case. From these results we shall first calculate the dielectric constant of water, using equations I and II, and the relation between fringe shift f and change in the refractive index Δn, namely

$$\Delta n = \frac{\lambda f}{2l}.$$

From these equations we find as a result of substitution that

$$f = \frac{(D-1)(D+2)(n^2-1)(n^2+2)}{144\pi n\lambda} \cdot \frac{21XV^2}{d^2},$$

where

$$d = 1.8 \text{ cm.},$$
$$l = 10.0 \text{ cm.},$$
$$X = 50 \times 10^{-12},$$
$$n = 1.3330,$$

and

$$\lambda = 5.416 \times 10^{-5} \text{ cm.}$$

Taking the value for f corresponding to a given value for V^2, e.g.,

$$V^2 = 2.5 \times 10^7/9 \times 10^4 = 2.5/9 \times 10^3 \text{ e.s.u.},$$

we find for $(D - 1)(D + 2)$ the value

$$(D - 1)(D + 2) = 77.3 \pm 3.1 \qquad \text{at } 23^\circ \text{ C.}$$

in good agreement with the theoretical value of

$$D = 81.0 \text{ for water.}$$

In calculating these results a correction was applied to the values of the voltages given above since we were using alternating current in these experiments. This correction amounted to assuming that the edge of the fringes moved an amount equal to that produced by a steady applied potential whose value was the same as the maximum voltage in the cycle. As an additional check on this point, the dielectric constant of ethyl alcohol was measured: the value for this liquid was found to be

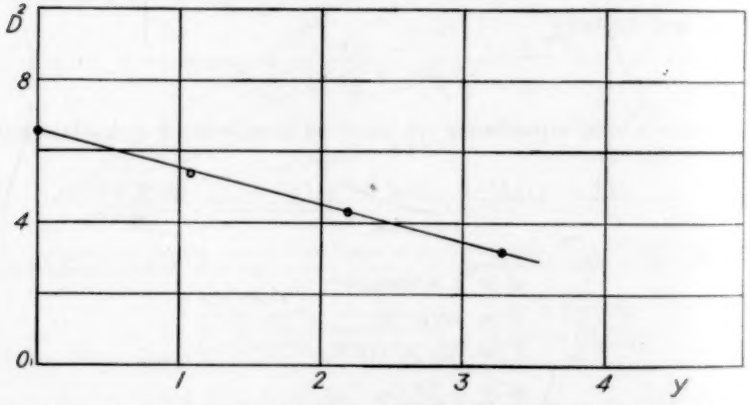
$$D = 24.0 \pm 1.0 \qquad \text{at } 23^\circ \text{ C.,}$$

while the value determined by other methods gave

$$D = 25.8 \qquad \text{at } 20^\circ \text{ C.,}$$

which is fairly good agreement.

FIG. 3.



In this figure, the ordinates represent the squares of the dielectric constant $D^2 \times 10^{-2}$, the abscissæ the concentrations $y \times 10^{-2}$ mol./l.

Having determined the dielectric constant of water from this graph, the determination of the dielectric constant of the

solutions of various concentrations is a simple matter since the refractive index and coefficient of compressibility are practically independent of the solution, provided the concentration is small. Thus the dielectric constant D of the solution is related to the fractional fringe shift f by the equation

$$D^2/D_{H_2O}^2 = f/f_{H_2O} \qquad \text{for any given voltage.}$$

The values of the dielectric constant squared obtained in this manner from Fig. 2 are plotted against the concentration in Fig. 3.

From the graph we see that the relationship between D^2 and y, the concentration, is linear so that we can write for the equation expressing the dependence of D^2 on y, the relation

$$D^2 = D_0^2(1 - \alpha y),$$

where $D_0^2 = (81.0)^2$, the dielectric constant of pure water,

and $\alpha = 15.7$ from the experimental curve.

For small concentrations, where it is legitimate to neglect the higher powers of y than the first, we can write for this relationship

$$D = D(1 - 7.85y).$$

The accuracy of the values obtained is determined by the accuracy with which we can measure the fringe shifts: in these experiments the maximum error due to this cause was less than 4%, so that the value of $\alpha/2$ is correct to the same maximum deviation

$$\frac{\alpha}{2} = 7.85 \pm .31.$$

Pennsylvania Day. An Act of the General Assembly of Pennsylvania approved March 9, 1927, directs that the Governor shall annually issue his proclamation designating Pennsylvania Day to be observed as a patriotic day. Pennsylvania Day shall be March 4, unless that date falls on Saturday or Sunday, when the preceding Friday or the following Monday may be designated. The act also directs that exercises be held in the public schools on that day with reference to the granting of the Charter of Pennsylvania to William Penn, and the life and principles advocated by Penn in founding Pennsylvania. The Department of Public Instruction of the Commonwealth of Pennsylvania has issued a brochure of 52 pages on Pennsylvania Day. It contains a biography of William Penn, a section on "Some Pennsylvania Initiatives," and chapters on agriculture, art, birds, education, forests, highways, historic shrines, industries, literature, mammals, music, and science in Pennsylvania. Suggestions for celebration of Pennsylvania Day are included. J. S. H.

THE COVERING POWER OF PHOTOGRAPHIC SILVER DEPOSITS.*

Part I.

BY

S. E. SHEPPARD AND A. BALLARD

Kodak Research Laboratories.

THE relation of the obscuring power of photographic silver deposits to the amount of silver per unit area has been the subject of several researches since the time of Hurter and Driffield's *Photochemical Investigations*.[1] They defined the density as

$$D = \log_{10} O = \log_{10} \frac{1}{T} = \log_{10} \frac{I_0}{I},$$

where O = opacity,

$$T = \text{transparency} = \frac{I}{I_0} = \frac{\text{light transmitted}}{\text{light incident}}.$$

Since the developed silver image partly scatters some of the light, it is necessary [2] to distinguish between *diffuse* density $D_{\#}$ measured for light already completely scattered and $D_{//}$, i.e., density measured for a parallel beam of light. The value of $D_{\#}$ may be determined by placing the image in contact with a piece of opal glass, so that the light incident is thoroughly diffused.[3] Hurter and Driffield obtained the definition of density from the assumption that the silver particles in a developed image could be regarded as obeying the Lambert-Beer absorption law. Consequently the density $D_{//}$ should be proportional to the mass of silver per unit area. They found

* Communicated by the Director and published as Communication No. 338 from the Kodak Research Laboratories.

[1] *J. Soc. Chem. Ind.*, 9, No. 5 (1890).

[2] A. Callier, *Phot. J.*, 49, 200 (1909).
F. F. Renwick, *Phot. J.*, 52, 250 (1912).

[3] It is realized that this does not give so complete diffusion as an integrating sphere. *Cf.* A. J. Bull and H. M. Cartwright, *Phot. J.*, 49, 177 (1925).

this to hold experimentally for one emulsion over a range of density 0.5 to 2.0, and for another for a range 0.75 to 2.5, in both cases with the same developer, ferrous oxalate. J. M. Eder [4] confirmed this for another emulsion for the range 0.5 to 2.0, also with ferrous oxalate. Sheppard and Mees [5] found the relation to hold quite closely for a slow emulsion, also with ferrous oxalate, over a range 0.5 to 3.5.

This constant proportionality may be expressed in the form

$$P = S/D,$$

where S = mass of silver per dcm.^{2},
D = density,

and the term *photometric constant* was applied by Sheppard and Mees to the ratio P.

In 1923 Scheffers [6] published some experimental results on this subject in a paper on solarization. He found fairly good constancy for P over a range of density from 0.08 to 1.12, but observed that the value of P of the solarized image became progressively smaller as solarization advanced. This he attributed to solarization being a development phenomenon, smaller silver grains being produced as solarization advanced.

In a theoretical paper P. G. Nutting [7] showed on the basis of probability considerations that the transparency of a multiple layer of n grains of average projective area a would be

$$T_m \equiv (1 - a_1n_1)(1 - a_2n_2) \cdots (1 - a_mn_m),$$

the corresponding *absorption* B_m being given by $B_m = 1 - T_m$. If the layers are alike in number and size of grain, the transparency would be

$$T_m = (1 - an)^m$$

corresponding to Lambert's law.

---

[4] "Handbuch der Phot.," 3d Edit., p. 222 (1903).

[5] "Investigations on the Theory of Photographic Process" (Longmans, Green, and Co., London, 1907), p. 41.

[6] *Zeit. physik. Chem.*, 20, 120 (1923).

[7] *Phil. Mag.*, 26, 421 (1913).

Density D in this case $= -m \log (1 - an)$ but, if "A is so small that the overlapping of grains is negligible,"

$$D = mA = mna.$$

Further, "if the film is m layers deep, $mn = N$ is the total number of grains per unit area, and S the mass of silver $= cNa^{3/2}$, the constant c involving the specific gravity of the silver and other factors.

The photometric constant (P) is

$$P = \frac{M}{D} = \frac{cNa^{3/2}}{Na} = c\sqrt{a}$$

if the overlapping of grains is negligible. Hence, to a first approximation P should be independent of N, i.e., of exposure and development, but should "vary among different brands of plates in proportion to the mean diameter."

Higson,[8] applying considerations similar to those used in deriving the Lambert-Beer law of absorption, obtains the approximate relation

$$D = Na,$$

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In a paper by Meidinger[10] in 1924, a number of experimental investigations on the photometric equivalent were

[8] *Phot. J.*, **44**, 161 (1920).

[9] *Cf.* Wightman, Trivelli, and Sheppard, *J. Phys. Chem.*, **28**, 529 (1924); Davidson, *Phot. J.*, **49**, 19 (1925).

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reported. Meidinger found, using a metol developer, that the value of P was independent of exposure for the same emulsion and development. With emulsions of different grain size, however, he found that P decreased, or the covering power increased, with decreased size of grain, in qualitative agreement with Nutting's conclusion. He does not give any values of the average diameter of the developed grains in each emulsion but the ranges of variation were as follows:

Emulsion.	Fast Large Grain.	Process Fine Grain.	Lantern Very Fine Grain.
$P = S/D$	0.0182	0.0100	0.0063
Covering Power $= 1/P$	5	9.1	10.5

EXPERIMENTAL.

In most of the experimental work on the photometric constant so far, the density appears to have been varied by altering the exposure, development being generally carried to the limit or nearly so. The early investigations of Sheppard and Mees [11] on the microscopy of development showed that the average size of the developed grain increases during development; it would be expected from this that the photometric constant would depend very much upon the time of development. In commencing an investigation of the covering power of the developed image, it was felt that satisfactory advances could be made only by developing a method which permitted the analytical determination of the silver on the small areas of the individual exposures on sensitometric strips.

This means, for the usual types of sensitometers, determination of the silver on areas of about 1 cm.^{2}. Our first work was devoted, therefore, to the study of microchemical methods of silver determination. The methods used by earlier investigators, operating on rather large plates, were either gravimetric or volumetric methods not applicable, as operated, to extremely small amounts of silver.

[11] "Investigations on the Theory of the Photographic Process" (Longmans Green, and Co., London, 1907).

The amounts of silver which have to be determined under these conditions are very small. Assuming a value of $P = \frac{\text{gms. silver per 1 cm.}^2}{\text{density } D = 1} = 0.01$, we should have the following:

D	Ag per 100 cm.² gms.	Ag per 1 cm.² mg.
0.01	0.0001	0.001
.1	.001	.010
1.0	.01	.100

It was felt that the method to be used should be capable of determining 0.010 mg. silver, with an error of the order of 2 to 3 per cent., that is, it would be capable of evaluating the covering power on photographic areas of 1 cm.² for densities down to 0.10, but for densities lower than this, correspondingly larger areas would be necessary.

The methods investigated were:

(*a*) Nephelometric determination of silver as silver chloride or silver bromide.

(*b*) Colorimetric determination of silver as colloid silver.

(*c*) Colorimetric determination of silver as silver sulfide.

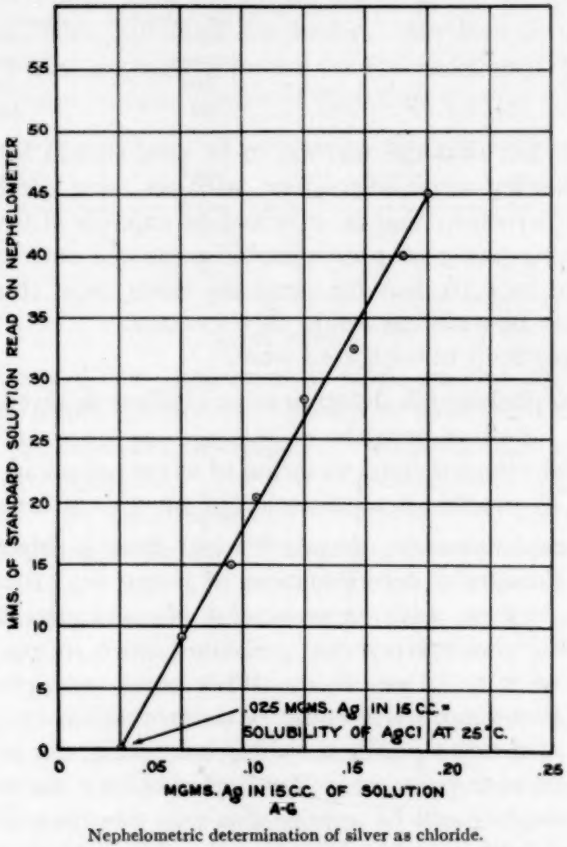
The nephelometric method [12] with silver precipitated as chloride permits a determination of 0.025 mg. silver in a volume of 15 c.c. with an error of 5 per cent.; at 0.10 mg. the error is about 8 per cent., and around 0.20 mg. can be reduced to 1 to 2 per cent. With silver precipitated as bromide, 0.005 mg. silver could be determined in 15 c.c. with an error of 8 to 10 per cent. Above 0.10 mg. the error can be reduced to 1 per cent. The nephelometric method with silver bromide could be applied down to densities of 0.1 per 1 cm.² but with an error of the order of 8 per cent.; it was decided to secure somewhat higher precision than this on the actual analytical procedure for the estimation of silver, since other errors (*vide inf.*) might readily add an equal or greater percentage error to this.

A colorimetric method of determining small amounts of

[12] *Cf.* also S. E. Sheppard, "Gelatin in Photography," Vol. I. (Eastman Kodak Co., Rochester, N. Y., 1923).

silver as colloidal silver was proposed by G. Stafford Whitby.[13] Silver dissolved as silver nitrate is reduced to colloidal silver by an alkaline reducing solution. Although this reaction is

FIG. 1.



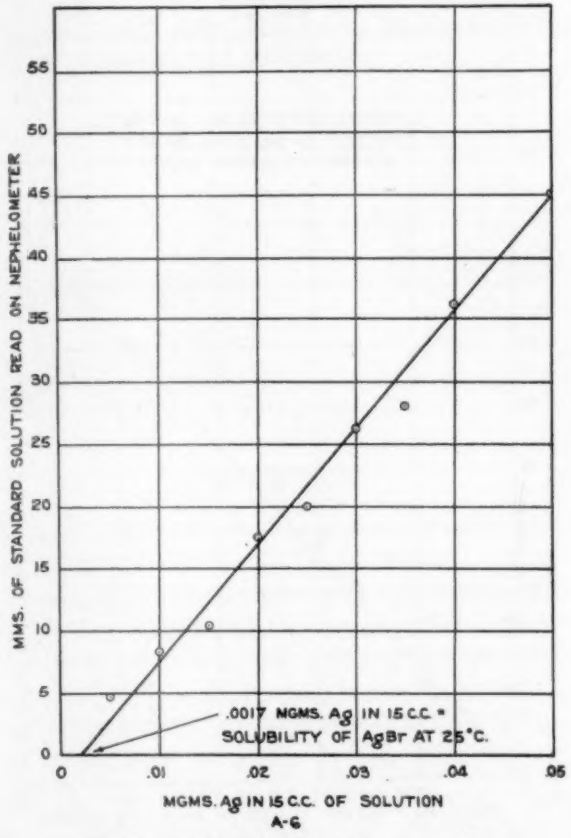
Nephelometric determination of silver as chloride.

very sensitive, giving definite evidence for 1 part silver in 20,000,000, we were not able to make quantitative use of it for our purpose. The tint of the colloidal silver solution was decisively determined by the initial concentration of the silver, so that accurate colorimetric comparison of an unknown with a standard sol was not possible.

[13] 7th International Congress Appl. Chem., 1909, Sect. 1, p. 12.

A colorimetric method in which the silver is converted to a silver sulfide hydrosol and compared with a standard was investigated; with a volume of 25 c.c., the method was

FIG. 2.



Nephelometric determination of silver as bromide.

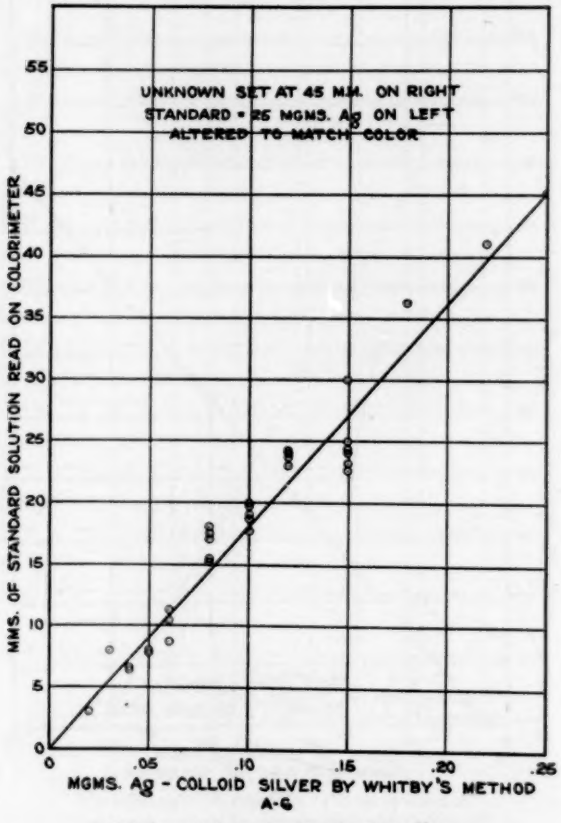
available only down to 0.01 mg. silver, the intensity of coloration being inadequate below a concentration of this order.

A method based on this colorimetric comparison was used by K. C. D. Hickman [14] but the accuracy reached was not

[14] *Phot. J.*, **62**, 512 (1922).

sufficient for our purpose. It was pointed out by Hickman that the method might be refined to give greater accuracy. Since the limit in the direction of sensitivity was set by the concentration, it was decided to try a microcolorimeter.

FIG. 3.



Colorimetric determination of colloid silver.

Using an instrument working with 2 c.c., we were able to develop a method of sufficient sensitivity to determine 0.002 mg. silver with a very fair degree of accuracy.

The procedure adopted was developed initially for use with film, owing to the greater convenience in cutting out small areas without first stripping the emulsion from the

support. The small pieces of exposed, developed, fixed and well-washed film were punched out of the sensitometer fields with a hollow steel punch, giving less than a square cm. in area (*cf.* Table I). The reproducibility of the areas secured in this way was less than 1 per cent. Thus, from a piece of film weighing 1.0205 gms. and being 29.51 sq. cms. in area, 9 pieces were punched and weighed.

TABLE I.

No.	Wt.	Δ	% Δ
1	0.0195 g.	−0.0001	−0.5
2	.0197 g.	+ .0001	+ .5
3	.0196 g.	.0	0
4	.0197 g.	+ .0001	+ .5
5	.0196 g.	.0	0
6	.0196 g.	.0	0
7	.0196 g.	.0	0
8	.0194 g.	− .0002	−1.0
9	.0197 g.	+ .001	+ .5
Av.	0.0196 g.		± .33

Area 0.567 sq. cm.

At first the pieces were placed individually in small flat-bottomed vials, and nitric acid (conc.) added. After standing to destroy partially the gelatin and completely dissolve the silver, water was added and the silver sulfide color developed by the addition of an alkaline sodium sulfide solution. On comparison in a microcolorimeter, it was found that the depth of color was approximately proportional to the silver content, but experiments with silver-free, blank film showed that the blank color, due probably to the xantho-protein reaction, was sufficient to cause appreciable error, particularly for small amounts of silver.

A modification was made, which consisted in treating each small piece of film with a few drops of strong sulfuric acid. The test was allowed to stand 5 minutes, to partial destruction of the gelatin and to dispersion of the silver. A few drops of 1 per cent. bromine water were then added, and the test allowed to stand until the silver was completely brominated.

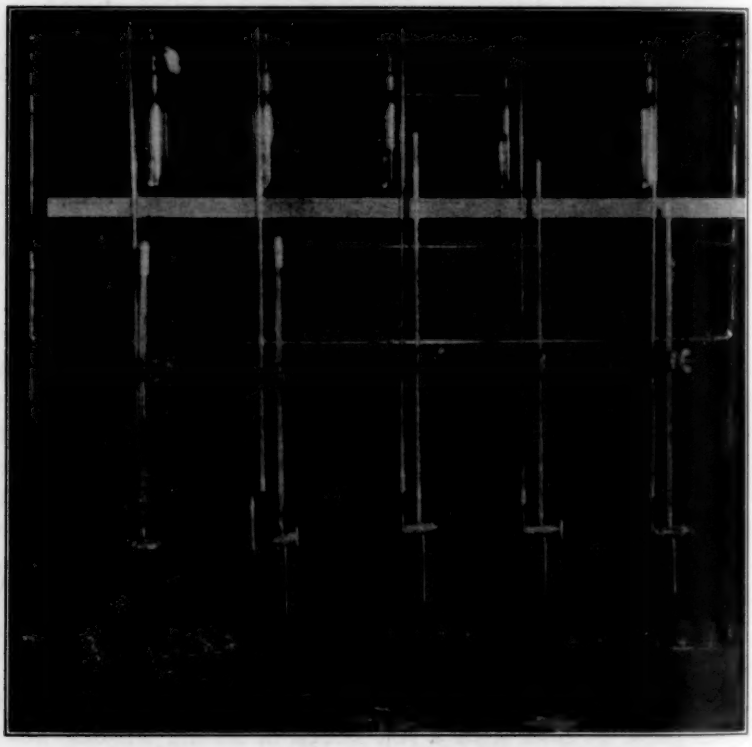
Aqueous ammonia was then added to dissolve the silver bromide formed, then the silver sulfide color was developed with sodium sulfide solution, and the color intensity compared with a standard in the microcolorimeter.

DETAIL OF PROCEDURE.

The reagents employed are:

Sulfuric acid (puriss.), 2 parts to 1 part water.
Bromine water, 1 per cent.

FIG. 4.



Reagent dispensing set-up.

Ammonia aq. fortiss.
Sodium sulfide (puriss.), 1 per cent. solution.

Apparatus required:

(*a*) 3 2-c.c. micro-burettes graduated in 2/100.
(*b*) 1 5-c.c. micro-burette graduated in 5/100.
(*c*) 1 10-c.c. micro-burette graduated in 5/100.
(*d*) 1 stand with 12 flat-bottomed ½-oz. vials.
(*e*) 1 microcolorimeter and illuminator.

The burettes are permanently attached to the reagent bottles.

The arrangement shown has proved very convenient when a large number of determinations are required. The microcolorimeter used was a Bausch and Lomb direct reading instrument (of the Dubosc type) which the makers modified for us for microchemical work by replacement of the regular plungers and vessels by special small plungers and vessels.

In the past, inadequate attention to the illumination has reduced the value of colorimeters in chemical analysis. The special illuminator provided with the instrument gives very even and satisfactory illumination. The instrument reads to 0.1 mm. on a cylinder of *ca.* 30 mm. height, taking a volume of 2 c.c.

Preparation of Samples:

After development and washing, the film was doubly fixed in fresh 25 per cent. hypo solution, thoroughly washed, and dried. Conditioning to a constant humidity of 50 per cent. R. H. at 70° F. is to be recommended before cutting out the test areas. These are punched out as described, and usually 10 *pieces* (test pieces) at a time for simultaneous analysis, the dispensing of each reagent being effected on the series of vials in the rack.

Procedure:

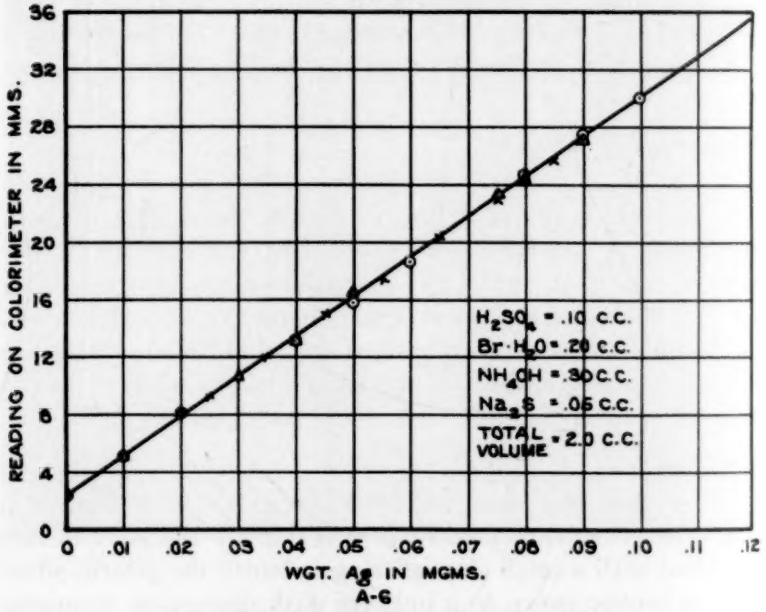
After each test piece has been placed at the bottom of a vial, 0.10 c.c. sulfuric acid reagent is run in; the piece of film is rubbed with a small glass stirring rod until the gelatin-silver layer is broken down to a uniform dark dispersion, requiring about 5 minutes. From burette (*b*) 0.10 c.c. bromine water is dispensed, when the silver is completely brominated to a

white suspension. There is then added a quantity of water to make up the volume to (V c.c. − 0.4 c.c.) where V c.c. is the selected dilution volume (see Fig. 1). The residual 0.4 c.c. is made up first by dispersing 0.3 c.c. ammonia aq. from burette (*c*), then 0.1 c.c. of sodium sulfide reagent from burette (*a*) into each vial. The yellow solutions are then transferred to colorimeter cups and the color compared with the standard. The latter is prepared by following the same procedure with an equal-sized piece of doubly fixed and washed, unexposed, undeveloped film, but adding a definite amount of silver nitrate or silver sulfate solution.

Colorimetric Determination:

The unknown is placed on the left side of the colorimeter, set at 30 mm., the standard on the right hand side, and the plunger on the standard side adjusted to color match. The

FIG. 5.



Microcolorimetric determination of silver as silver sulfide.

average of 3 readings is taken and converted to mg. silver

by reference to a large carefully drawn calibration curve or by using the equation of this, which is linear in form. The calibration curve is reproduced in the figure and shows the linear relation between color strength and silver content.

COMPARISON OF COLORIMETRIC AND GRAVIMETRIC METHODS.

Although the calibration curves for the microcolorimetry of silver as sulfide demonstrate its accuracy for the determination of silver from silver nitrate (or sulfate), it might be possible that the compensation introduced by the blank film was not sufficient to guarantee that the method is satisfactory for silver images. We made, therefore, a direct comparison of the silver per unit area on large film pieces of 3 different densities (*a*) by the colorimetric method, (*b*) by dissolving the silver, depositing electrolytically, and weighing. The density measurements were checkered over each sheet; they were very uniform [15] and the averages taken.

TABLE II.

No.	Density.	Method.	Area for Analysis.	Mg. Ag_2 Found per $cm.^2$.
1	0.53	(*b*) gravimetric	440 $cm.^2$	0.0112
		(*a*) microcolor.	.567 $cm.^2$	.0109
2	1.05	(*b*) gravimetric	450 $cm.^2$	.0187
		(*a*) microcolor.	.567 $cm.^2$	.0191
3	1.97	(*b*) gravimetric	460 $cm.^2$	.0271
		(*a*) microcolor.	.567 $cm.^2$	.0276

These results and others show that the microcolorimetric method gives results agreeing well with a direct gravimetric method applied to the developed silver image. The limit to which the micro-method with silver sulfide could be used was estimated as follows:

Amount of Silver.	*D.*	Reading.	Reading Per Cent.	Per Cent. Error.
0.001 mg.	0.01	2.55 mm.		± 10
.0025 mg.	.04	3.00 mm.	0.01	±0.5
.01 mg.	.10	5.00 mm.	.01	±0.2

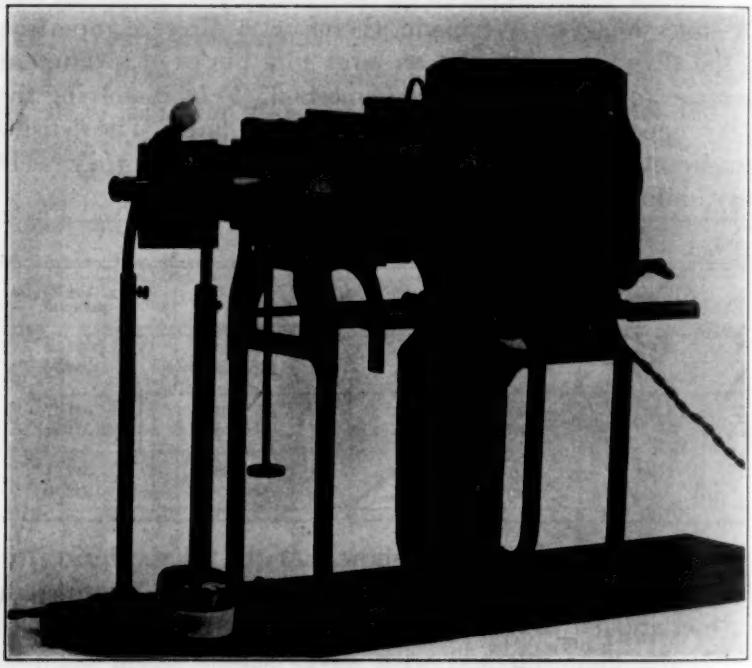
[15] For density measurements see later.

Below 0.0025 mg. silver the uncertainty of reading and comparison increases very rapidly and, while determinations can be made down to 0.001 mg. silver, the uncertainty is too large for the values to have much significance.

DENSITY MEASUREMENTS.

The accuracy with which the ratio D/M can be determined depends equally upon the accuracy of the silver analysis and upon that of the density measurements. The subject of

FIG. 6.



Arrangement of Martens photometer as densitometer.

densitometry and the differences between instruments have been very fully discussed in recent years, yet without any complete agreement on standardization being reached.[16] In the present case, and for the preliminary measurements here submitted, the method was as follows: density $D_{\#}$ was read in contact with opal glass on a Martens photometer (Fig. 6).

[16] *Phot. J.*, 49, 164 (1925).

This instrument was carefully calibrated against the Jones densitometer,[17] and after some readjustment brought to agree with the Jones instrument up to a density of 4.70, supplementary density being used above 2.5.

The area of plate or film covered by the Martens instrument is about 0.2 mm.^{2}. Four readings were taken at different points over the area of *ca.* 0.6 mm.^{2}, and the average used. It is planned in some further work on the subject to integrate the whole area optically and further correlate both the projection density and the diffuse density with mass of silver.

EXPERIMENTAL RESULTS.

Results with Eastman *Commercial* film and *Process* film are given in the following tables and curves. The developer used was:

p-Aminophenolhydrochloride	0.7275 gm.
Sodium sulfite	5 gms.
Sodium carbonate	5 gms.
Water	to 100.0 c.c.

The temperature was 25° C. and the films were brushed by hand during development. After fixing and washing they were dried and kept at constant humidity R. H. 50 per cent. at 70° F. The following tables summarize the results.

[17] L. A. Jones, *J. Opt. Soc. Amer.*, 7, 231 (1923).

TABLE III.

Series 47.—Process No. 8103. P. A. P. Developer.

$$\text{C. P.} = \text{Cov. Power} = \frac{1}{\text{P. E.}}.$$

No.	*1 min. development.*				*2 min. development.*			
	Log *E.*	Dens.	Ag per 100 sq. cm. in mgs.	C. P.	Log *E.*	Dens.	Ag per 100 sq. cm. in mgs.	C. P.
1	0.0	0.09	2.12	42.5	0.0	0.21	4.58	45.8
2	.3	.21	3.70	55.9	.3	.35	7.58	46.9
3	.6	.34	6.00	55.9	.6	.53	11.65	45.4
4	.9	.52	7.93	65.4	.9	.89	14.9	59.8
5	1.2	.68	9.08	74.6	1.2	1.13	17.55	64.5
6	1.5	.80	10.15	78.8	1.5	1.34	19.7	68.0
7	1.8	.93	10.93	84.7	1.8	1.58	21.3	74.6
8	2.1	1.07	11.8	93.5	2.1	1.87	23.1	81.2
9	2.4	1.14	12.95	87.0	2.4	2.07	23.4	88.4
	4 min. development.				*8 min. development.*			
1	0.0	0.38	9.17	41.5	0.0	0.62	16.7	37.0
2	.3	.62	13.2	47.	.3	.93	21.7	42.9
3	.6	.89	18.45	48.3	.6	1.16	25.6	45.5
4	.9	1.47	26.6	55.2	.9	1.59	34.4	46.3
5	1.2	1.83	32.6	56.8	1.2	2.28	45.0	50.8
6	1.5	2.26	37.4	60.6	1.5	3.11	53.8	57.8
7	1.8	2.82	39.8	70.9	1.8	4.15	62.8	66.2
8	2.1	3.18	41.6	76.3				
9	2.4	3.82	45.8	83.3				

TABLE III (*Continued*).

Series 47.—Continued.

No.	*16 min. development.*			
	Log *E.*	Dens.	Ag per 100 sq. cm. in mgs.	C. P.
1	0.0	1.01	29.4	34.3
2	.3	1.31	36.7	35.7
3	.6	1.62	42.8	38.0
4	.9	2.22	51.2	43.5
5	1.2	2.91	59.2	49.0
6	1.5	3.84	66.5	57.8

TABLE IV.

Series No. 85.—Comm. Film, P. A. P. Non-Intermittent.

No.	*1 min. development.*				*2 min. development.*			
	Log *E.*	Dens.	Mass Ag mgs. per 100 sq. cm.	C. P.	Log *E.*	Dens.	Mass Ag mgs. per 100 sq. cm.	C. P.
1	0.0	lost						
2	.3	0.14	2.6	53.7	0.3	0.15	3.03	49.5
3	.6	.27	4.3	63.5	.6	.27	4.85	55.5
4	.9	.36	5.7	62.9	.9	.42	8.15	51.6
5	1.2	.48	6.76	70.9	1.2	.60	11.96	50.2
6	1.5	.61	8.1	76.7	1.5	.81	11.2	71.4
7	1.8	.76	9.7	78.7	1.8	1.02	13.5	75.2
8	2.1	.88	9.6	92.5	2.1	1.23	14.9	82.6
9	2.4				2.4	1.48	15.9	92.6
	4 min. development.				*8 min. development.*			
1	0.0	0.15	3.2	46.7	0.0	0.23	6.24	36.8
2	.3	.25	5.37	46.5	.3	.35	9.0	38.8
3	.6	.41	8.3	49.3	.6	.54	13.5	40.0
4	.9	.59	12.8	46.2	.9	.81	18.4	44.1
5	1.2	.85	16.0	53.2	1.2	1.09	23.4	46.5
6	1.5	1.19	21.0	56.8	1.5	1.50	28.6	52.4
7	1.8	1.55	25.7	60.2	1.8	1.86	34.7	53.7
8	2.1	1.85	30.9	59.9	2.1	2.32	41.2	56.2
9	2.4	2.32	34.7	67.1	2.4	2.84	45.6	62.5
10					2.7	3.36	50.4	66.7

TABLE IV (*Continued*).

Series No. 85.—Continued.

No.	*16 min. development.*			
	Log *E.*	Dens.	Ag Mass mgs. per 100 sq. cm.	C. P.
1	0.0	0.32	11.6	27.6
2	.3	.48	16.3	29.5
3	.6	.72	lost	
4	.9	.99	25.5	38.8
5	1.2	1.31	31.9	41.1
6	1.5	1.66	37.2	44.7
7	1.8	2.11	44.0	48.1
8	2.1	2.63	48.5	54.4
9	2.4	3.22	55.3	57.2

TABLE V.

Series 86.—Comm. Film, P. A. P.

No.	*2 min. development.*				*4 min. development.*			
	Log *E.*	Dens.	Mass Ag in mgs. per 100 sq. cm.	C. P.	Log *E.*	Dens.	Mass Ag in mgs. per 100 sq. cm.	C. P.
1	0.0				0.0	0.13	2.95	44.1
2	.3				.3	.23	5.2	44.3
3	.6	0.25	4.85	51.5	.6	.35	8.14	43.0
4	.9	.40	7.3	55.0	.9	.55	12.3	44.7
5	1.2	.57	10.0	57.2	1.2	.79	16.3	48.5
6	1.5	.76	11.8	64.5	1.5	1.10	20.8	52.9
7	1.8	.99	13.5	73.0	1.8	1.43	24.1	59.5
8	2.1	1.19	14.4	82.6	2.1	1.68	26.5	63.3
9	2.4	1.40	15.9	86.7	2.4	2.29	28.8	79.3
10	2.7	1.56	17.1	90.9				
	8 min. development.				*16 min. development.*			
1	0.0	0.20	4.94	40.5	0.0	0.27	8.5	27.1
2	.3	.32	8.32	38.5	.3	.42	12.8	32.7
3	.6	.49	11.7	41.8	.6	.63	17.7	35.6
4	.9	.70	17.3	40.3	.9	.89	23.2	38.3
5	1.2	.99	20.8	47.6	1.2	1.18	28.9	40.8
6	1.5	1.36	26.3	51.8	1.5	1.51	34.7	43.6
7	1.8	1.73	32.9	52.6	1.8	1.97	43.1	45.7
8	2.1	2.19	41.8	52.4	2.1	2.50	49.2	50.7
9	2.4	2.69	46.8	57.4	2.4	3.05	54.8	55.5
10	2.7	3.20	50.2	63.7	2.7	3.59	61.0	57.8

TABLE VI.

Series 87.—Process Film, P. A. P.

No.	*1 min. development.*				*2 min. development.*			
	Log *E.*	Dens.	Mass Ag mgs. per 100 sq. cm.	C. P.	Log *E.*	Dens.	Mass Ag mgs. per 100 sq. cm.	C. P.
3					0.6	0.07	0.95	73.5
4	0.9	0.06	0.87	69.0	.9	.15	1.73	87.0
5	1.2	.14	2.0	70.4	1.2	.28	3.81	73.5
6	1.5	.26	3.64	71.4	1.5	.50	7.8	64.1
7	1.8	.45	6.24	71.9	1.8	.82	12.6	64.9
8	2.1	.65	8.24	78.7	2.1	1.16	16.8	69.0
9	2.4	.84	10.0	83.4	2.4	1.49	20.5	72.5
10	2.7	1.02	11.8	86.2	2.7	1.71	23.2	73.5
	4 min. development.				*8 min. development.*			
2					0.3	0.16	3.12	51.3
3	0.6	0.13	2.0	65.3	.6	.26	5.2	50.0
4	.9	.25	4.16	60.2	.9	.44	8.5	51.8
5	1.2	.45	7.5	60.2	1.2	.72	13.7	52.6
6	1.5	.76	12.0	63.7	1.5	1.15	21.0	54.9
7	1.8	1.12	18.4	60.9	1.8	1.54	28.6	54.9
8	2.1	1.52	26.2	58.0	2.1	2.06	36.4	56.5
9	2.4	2.09	34.7	60.2	2.4	2.59	45.1	57.4
10	2.7	2.65	41.2	64.1	2.7	3.26	51.3	63.7

TABLE VI (*Continued*).

Series 87.—Continued.

No.	*16 min. development.*			
	Log *E.*	Dens.	Mass Ag mgs. per 100 sq. cm.	C. P.
2	0.3	0.34	7.46	51.8
3	.6	.44	10.6	41.7
4	.9	.65	17.5	37.2
5	1.2	1.00	23.9	41.8
6	1.5	1.50	35.9	41.8
7	1.8	1.96	42.3	46.3
8	2.1	2.50	50.4	49.5
9	2.4	3.11	58.6	53.2
10	2.7	3.74	66.6	56.2

TABLE VII.

Series No. 80.—P. A. P. Comm. Film. Non-Intermittent.

No.	*1 min. development.*				*2 min. development.*			
	Log *E.*	Dens.	Ag per 100 sq. cm. in mgs.	C. P.	Log *E.*	Dens.	Mass Ag 100 sq. cm. in mgs.	C. P.
1	0.0	0.18	3.98	45.3	0.0	0.38	6.7	55.9
2	.3	.27	4.37	61.3	.3	.47	7.6	62.1
3	.6	.37	5.29	70.0	.6	.62	8.46	73.0
4	.9	.46	5.48	85.4	.9	.73	9.26	78.7
5	1.2	.55	6.51	82.6	1.2	.89	10.25	87.0
6	1.5	.65	7.0	92.6	1.5	1.07	11.5	93.4
7	1.8	.74	7.3	101.0	1.8	1.22	11.8	103.0
8	2.1	.83	7.62	109.0	2.1	1.34	12.35	109.0
9	2.4	.87	6.9	126.0	2.4	1.45	12.2	118.0
	4 min. development.				*8 min. development.*			
1	0.0	0.56	12.8	43.8				
2	.3	.79	16.0	49.2				
3	.6	1.07	18.9	56.6	0.6	1.39	28.4	49.0
4	.9	1.33	20.0	66.6	.9	1.83	33.5	54.6
5	1.2	1.62	21.7	75.2	1.2	2.23	41.1	54.3
6	1.5	1.95	24.5	79.3	1.5	2.72	45.0	60.6
7	1.8	2.32	26.3	88.5	1.8	3.20	49.8	64.1
8	2.1	2.60	28.4	91.8	2.1	3.7	53.4	69.4
9	2.4	2.87	28.4	100.0				

TABLE VII (*Continued*).

Series No. 80.—Continued.

No.	*16 min. development.*			
	Log *E.*	Dens.	Mass Ag 100 sq. cm. in mgs.	C. P.
2	0.3	1.32	30.9	42.7
3	.6	1.78	37.0	48.0
4	.9	2.17	45.8	47.4
5	1.2	2.71	52.4	51.8
6	1.5	3.32	59.6	55.8
7	1.8	3.89	60.3	64.0

TABLE VIII.

Series 99.

No.	*1 min. development.*				*2 min. development.*			
	Log *E.*	Dens.	Ag per 100 sq. cm. in mgs.	C. P.	Log *E.*	Dens.	Mass Ag 100 sq. cm. in mgs.	C. P.
1	0.0	0.20	3.12	64.0	0.0	0.36	6.58	54.3
2	.3	.26	4.24	61.4	.3	.50	8.75	57.2
3	.6	.36	5.02	71.5	.6	.69	10.1	68.0
4	.9	.44	5.55	81.3	.9	.90	11.8	76.3
5	1.2	.54	5.98	90.0	1.2	1.11	13.0	88.5
6	1.5	.64	6.41	100.0	1.5	1.35	14.1	95.2
7	1.8	.76	7.11	107.5	1.8	1.51	14.4	105.0
8	2.1	.85	7.63	111.0	2.1	1.68	15.2	111.0
	4 min. development.				*8 min. development.*			
1	0.0	0.48	10.3	46.5	0.0	0.66	15.9	41.5
2	.3	.71	15.2	46.5	.3	1.00	21.0	47.6
3	.6	1.03	19.2	53.5	.6	1.45	29.6	49.0
4	.9	1.37	22.4	61.4	.9	1.92	37.5	51.3
5	1.2	1.69	24.6	69.0	1.2	2.51	44.9	55.9
6	1.5	2.04	28.3	72.4	1.5	3.06	49.2	62.1
7	1.8	2.38	29.5	80.6	1.8	3.56	52.8	67.1
8	2.1	2.70	30.7	87.7	2.1	4.07	54.6	74.6

GRAPHICAL REPRESENTATION.

There are several ways in which the analytical results can be graphically represented. We may in the first place plot the covering power, or its reciprocal, the photometric equivalent, against density. In this case, the present results show that this should be done for equal times of development, since exposure and development may not give the same covering

Fig. 7.

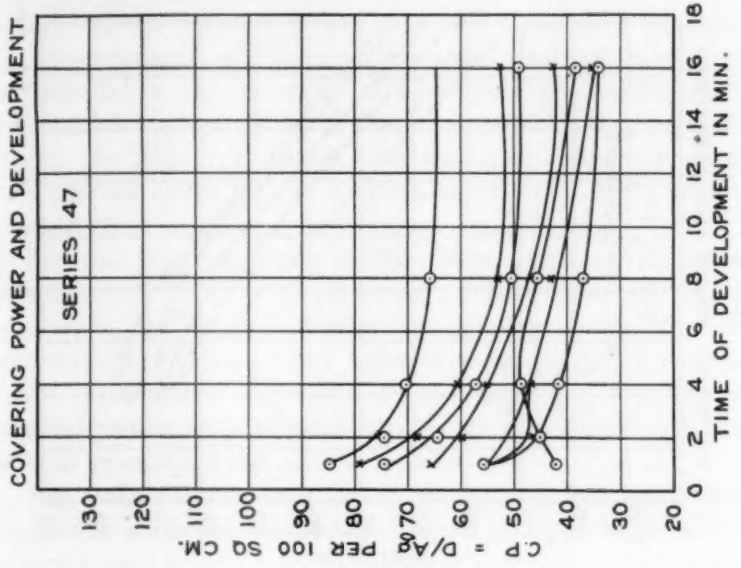

COVERING POWER AND DEVELOPMENT
SERIES 47
C.P. = D/Ag PER 100 SQ. CM.
TIME OF DEVELOPMENT IN MIN.
130
120
110
100
90
80
70
60
50
40
30
20
0 2 4 6 8 10 12 14 16 18

Fig. 8.

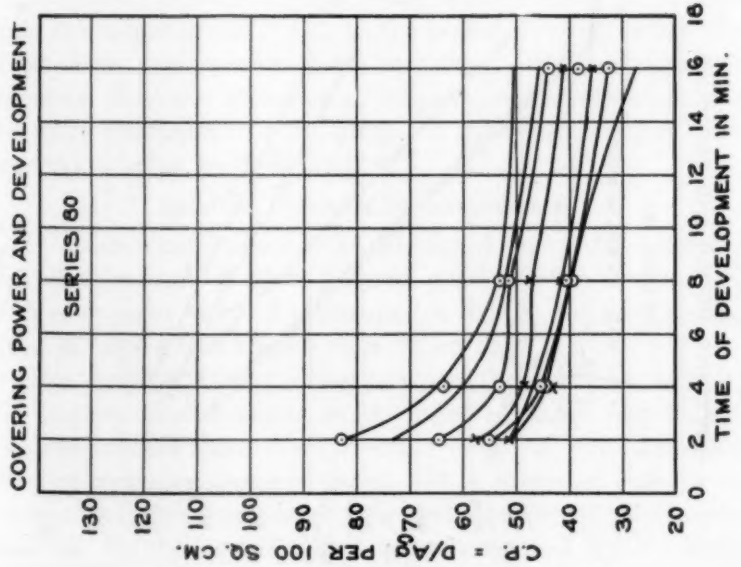

COVERING POWER AND DEVELOPMENT
SERIES 80
C.P. = D/Ag PER 100 SQ. CM.
TIME OF DEVELOPMENT IN MIN.
130
120
110
100
90
80
70
60
50
40
30
20
0 2 4 6 8 10 12 14 16 18

FIG. 10.

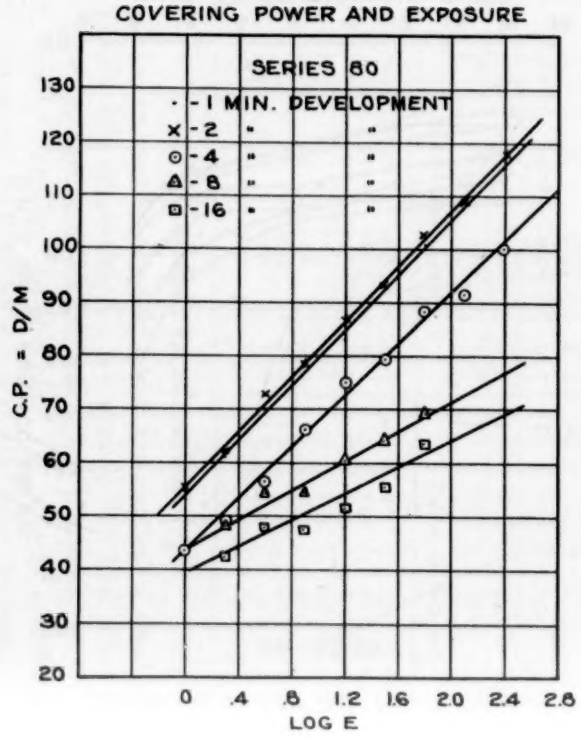
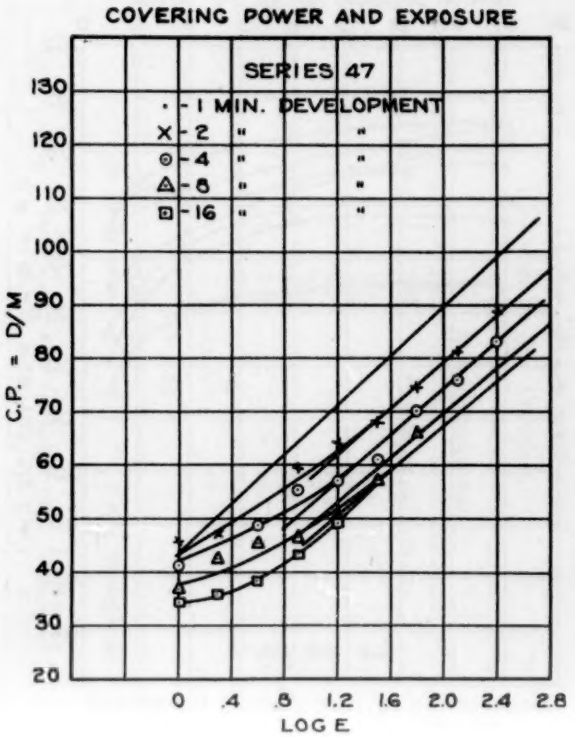

COVERING POWER AND EXPOSURE
SERIES 60
· - 1 MIN. DEVELOPMENT
× - 2 " "
⊙ - 4 " "
△ - 8 " "
⊡ - 16 " "
C.P. = D/M
130
120
110
100
90
80
70
60
50
40
30
20
0
.4
.8
1.2
1.6
2.0
2.4
2.8
LOG E

FIG. 9.


COVERING POWER AND EXPOSURE
SERIES 47
· - 1 MIN. DEVELOPMENT
× - 2 " "
⊙ - 4 " "
△ - 8 " "
⊡ - 16 " "
C.P. = D/M
130
120
110
100
90
80
70
60
50
40
30
20
0
.4
.8
1.2
1.6
2.0
2.4
2.8
LOG E

power. If the covering power were independent of exposure and development, all these values should fall on a straight line parallel to the abscissa. Under these conditions, more information is given by separating exposure and development effects. In Figs. 7, 8, 9 and 10 is shown the covering power D/M plotted against log E and against time of development respectively.

For the two emulsions studied here, the *covering power decreases with time of development;* this obtains for every exposure. The rate of change becomes less as the time of development increases, and there is some tendency for the curves for different exposures to run parallel. The fall in covering power with development is in agreement with the increase in average size of development grain.

The values of covering power plotted against log (exposure) show a distinct tendency to give straight lines, which become nearer together as development proceeds. The covering power tends to *increase* with increased exposure.

This effect is probably due to the *selective action* of exposure upon the larger grains,[18] i.e., to the higher average sensitivity of the larger grains in the same emulsion. We should expect, therefore, that the variation of covering power would be less, the more homogeneous the emulsion in regard to grain size, and this is being studied further.

CHEMICAL DYNAMICS OF DEVELOPMENT.

It is obviously possible to disregard the optical density and plot the mass of silver per unit area as a function of time of development, and of exposure (or log E). Examples are given in Figs. 11 to 16 and Figs. 17 to 19.

The formulation of equations for the reaction velocity will require modifications in the light of these results, but requires further data over a wider range of emulsions, developers, and development times. It is, however, sufficiently evident that development [19] is a pronouncedly topochemical reaction, in the classificatory sense proposed by V. Kohl-

[18] Wightman, Trivelli and Sheppard, *Phot. J.*, **49**, 134 (1925).

[19] And to some extent the formation of the latent image itself.

FIG. 11.

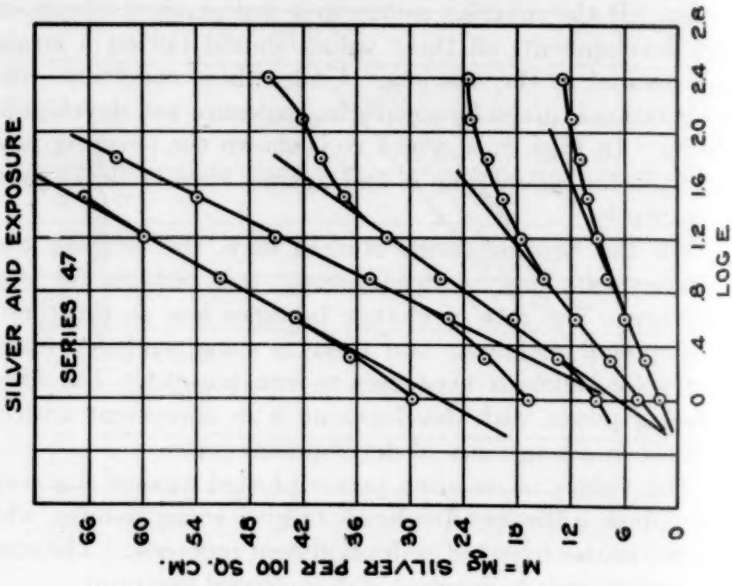

SILVER AND EXPOSURE
SERIES 47
M = Mg SILVER PER 100 SQ. CM.
0 6 12 18 24 30 36 42 48 54 60 66
0 .4 .8 1.2 1.6 2.0 2.4 2.8
LOG E

FIG. 12.

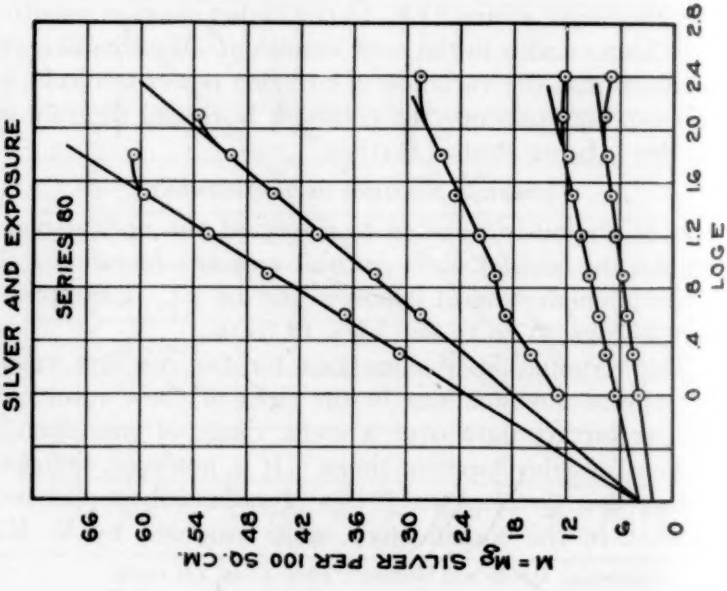

SILVER AND EXPOSURE
SERIES 80
M = Mg SILVER PER 100 SQ. CM.
0 6 12 18 24 30 36 42 48 54 60 66
0 .4 .8 1.2 1.6 2.0 2.4 2.8
LOG E

FIG. 13.

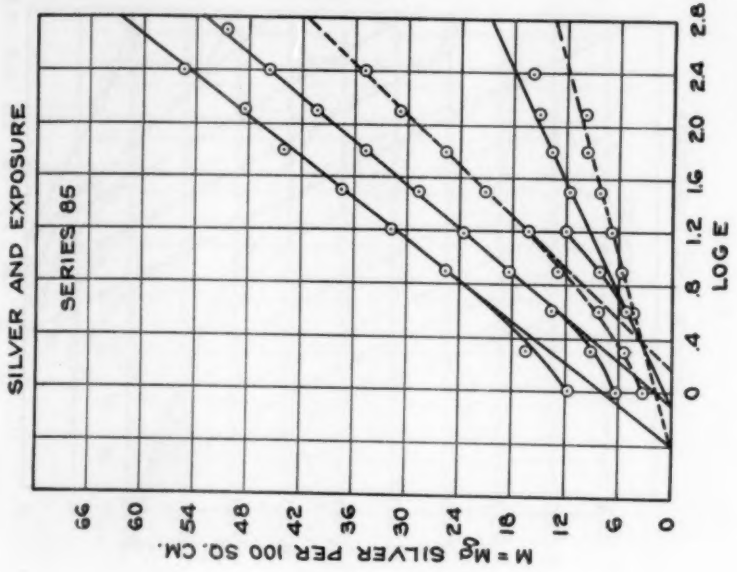

SILVER AND EXPOSURE
SERIES 85
M = Mg SILVER PER 100 SQ. CM.
LOG E
0
6
12
18
24
30
36
42
48
54
60
66
0
.4
.8
1.2
1.6
2.0
2.4
2.8

FIG. 14.

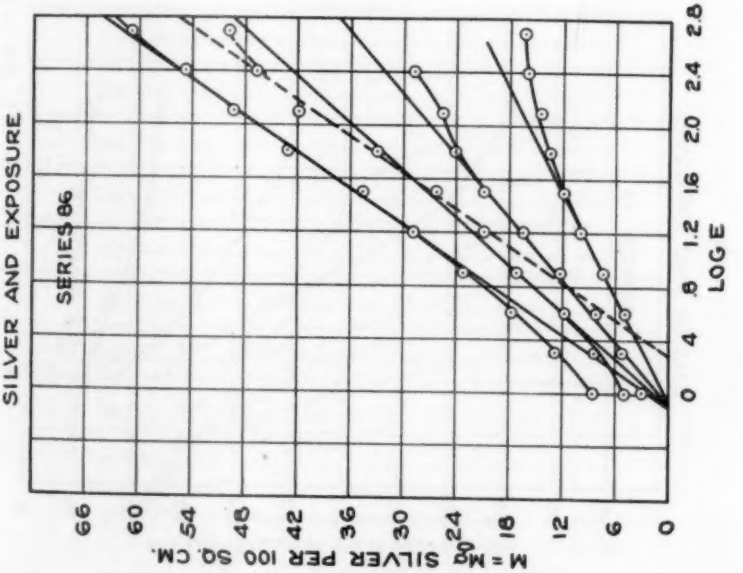

SILVER AND EXPOSURE
SERIES 86
M = Mg SILVER PER 100 SQ. CM.
LOG E
0
6
12
18
24
30
36
42
48
54
60
66
0
.4
.8
1.2
1.6
2.0
2.4
2.8

FIG. 15.

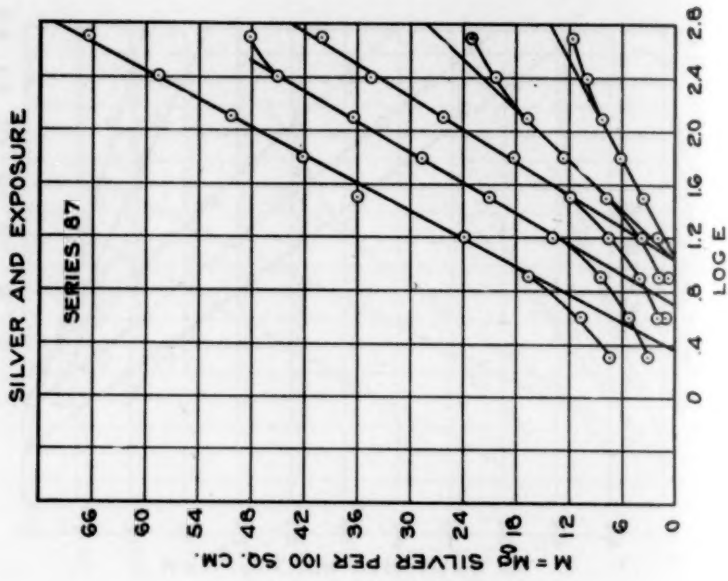

SILVER AND EXPOSURE
SERIES 87
M = Mg SILVER PER 100 SQ. CM.
LOG E
0
6
12
18
24
30
36
42
48
54
60
66
0
.4
.8
1.2
1.6
2.0
2.4
2.8

FIG. 16.

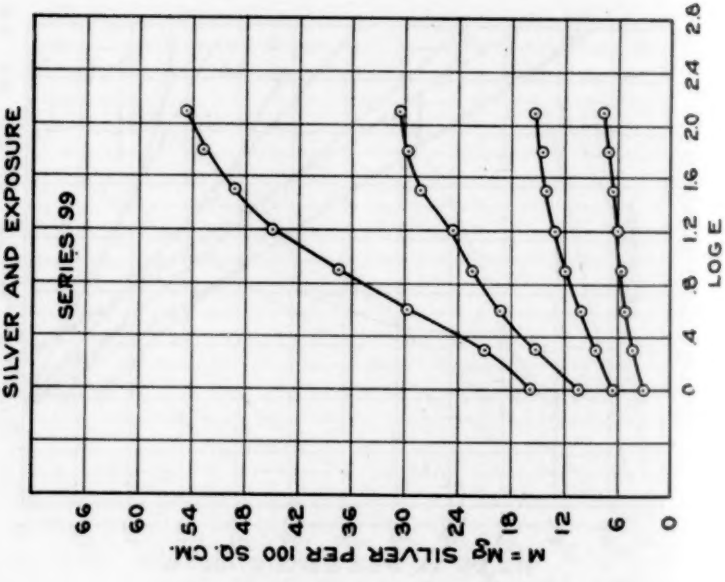
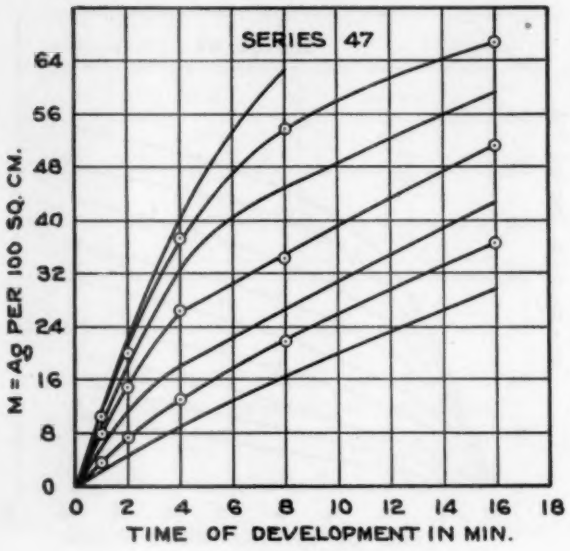
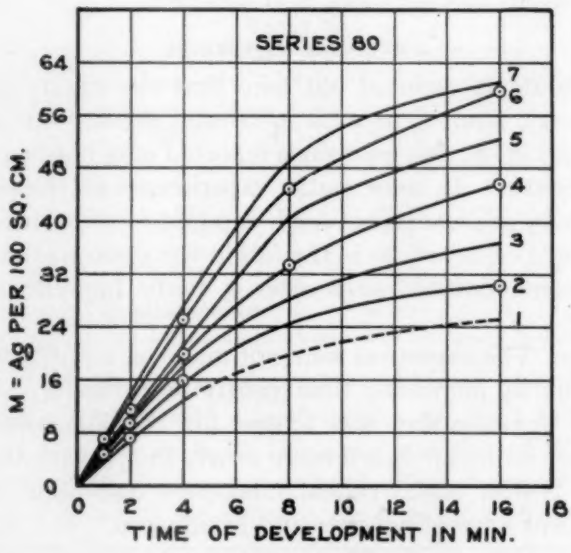

SILVER AND EXPOSURE
SERIES 99
M = Mg SILVER PER 100 SQ. CM.
LOG E
0
6
12
18
24
30
36
42
48
54
60
66
0
.4
.8
1.2
1.6
2.0
2.4
2.8

FIG. 17.



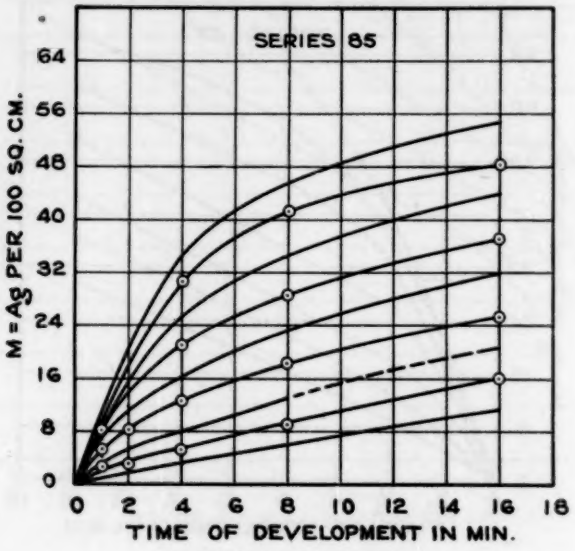
Mass of silver and development.

FIG. 18.



Mass of silver and development.

FIG. 19.



Mass of silver and development.

schütter.[20] A study of the covering power in relation to the microscopy of development is in progress.

EMULSION DIFFERENCES.

It should be pointed out here that the rapid fall in the photometric equivalent with increasing density due to exposure found in the two emulsions reported may not be generally characteristic. In some earlier experiments on the problems, in which large plates were used, exposed for increasing times, and developed nearly to γ, the fall in the photometric equivalent became notable only after a fairly high density was reached.

Note: The exposures were not made on a pure time scale, but partly by increasing time, partly by intensity. Also the time of development was longer for the last two values.

These results are much more nearly in line with the earlier ones of Hurter and Driffield, Sheppard and Mees, and the more recent ones of Scheffer and Meidinger.

[20] *Zeits. anorg. Chem.*, **105**, 35 (1918). *Lieb. Ann.*, **390**, 340 (1912); *ibid.*, **387**, 80 (1912).

TABLE IX.

	Eastman 33.		Eastman 40.	
	Density.	P. E.	Density.	P. E.
Increase of Exposure. ↓	0.44	0.0194	0.22	0.0198
	.53	.0197	.43	.0207
	.96	.0192	.82	.0202
	1.08	.0188		
	1.90	.0196		
	2.00	.0179	2.27	.0209
	2.75	.0164		
	3.69	.0159	3.18	.0166
	4.47	.0149	3.95	.0163
	4.64	.0140		

COVERING POWER OF FOG DEPOSITS.

The fact however that the covering power of the developed silver can be enormously affected by the factors,

grain size → sensitivity → exposure → development,

is very clearly brought out by an investigation of the covering power of "development fog" at different times of development.

TABLE X.

Time of Development.	Emulsion.	Commercial Film.		
	Density.	Gms. Ag per 100 cm.².	P. E.	C. P.
32 mins.	0.35	0.010	0.029	34.5
64 "	.78	.025	.032	31.2
128 "	1.24	.058	.047	21.3
256 "	1.34	.066	.049	20.8
1024 "	1.34	.078	.058	17.2
	Original emulsion	0.083		

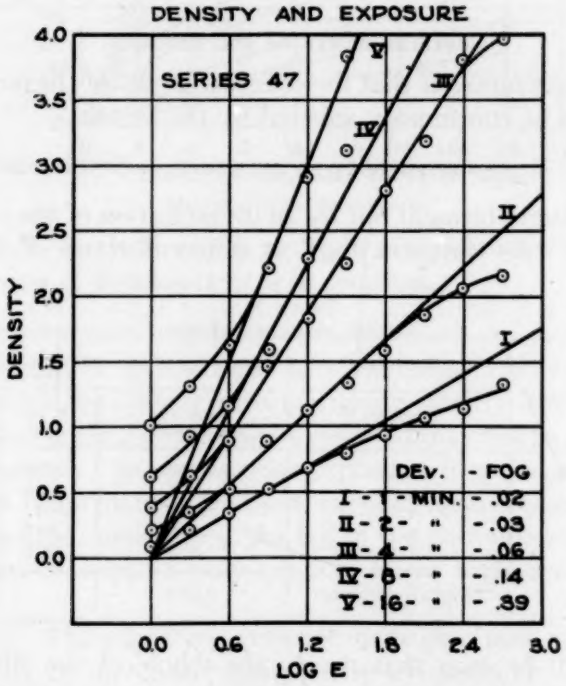
It will be seen that nearly the whole of the silver was finally reduced, but with a final density of only 1.34. Yet on sufficient exposure to light this same amount of silver gave a density approaching, or greater than, 6.00. From the figures in Table IV, it will also be seen that the developed image might have a covering power of 80, that is, up to 5 times as great as that of the "fog."

This effect cannot be due entirely to the "selective effect" by which fog commences more readily in the larger grains [21] but must also be connected with the influence of the individual rate of reduction of the grain, according to which, the slower the reduction, the more compactly the silver is deposited.

CHARACTERISTIC CURVE.

It is evident that the characteristic curve is still of the same form as when density is plotted, but the relations of a family of curves for different times of development may be

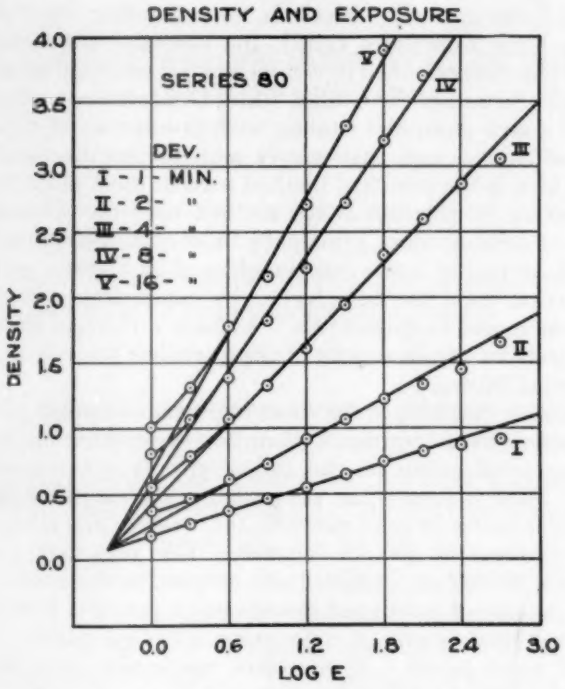
FIG. 20.



very different. From the results at present obtained, there appears a more pronounced tendency for the D: log E curves to give a common point of convergence of the straight line

[21] *Cf.* E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard, *Phot. J.*, 49, 134 (1925).

FIG. 21.



portions than for the M: log E curves. (Compare Figs. 11 to 16 with Figs. 20 and 21.)

ROCHESTER, N. Y.,
August 22, 1927.

Extraction of Volatile Oils.—U. S. Department of Agriculture, Technical Bulletin 16-T. Methods for extracting the volatile oils or, as they are sometimes called, the essential oils from various species of plants are divided into three main classifications, according to Arthur F. Sievers of the United States Department of Agriculture, author of a new pamphlet dealing with production of these oils in the United States, and particularly with the steam distillation of the oils which is the principal method used in the United States.

Extraction by solution is the method used for obtaining some of the more delicate odors, principally those of flowers, and the products are used mainly in the compounding of high-grade perfumes.

Extraction may also be achieved by expression, particularly of orange, lemon, and bergamot oils. As used in Europe, this method, too, demands an ample supply of cheap skilled labor, not available in the United States.

Turpentine distilling is the most important example of essential oil production by steam distillation, but since there are a number of separate publications on this industry, it is not covered in this bulletin. Next to turpentine, peppermint oil constitutes the largest volatile-oil industry in the United States, with an annual production of from 350,000 to 400,000 pounds. The principal production areas are in Michigan, Indiana, and on the Pacific coast. On the average, an acre of mint produces about 30 pounds of the essential oil, which is used largely as a flavoring agent for candies, chewing gum and tooth-pastes. It possesses medicinal qualities and is used extensively in medical practice.

In addition to peppermint, the crops cultivated for oils include spearmint, Japanese peppermint, which yields an oil rich in menthol, American wormseed, cultivated principally in Maryland, and wormwood, tansy, and dill.

Other oils of more or less commercial importance listed are sassafras, wintergreen, sweet birch, erigeron, witch-hazel, eucalyptus, and pennyroyal, which are extracted from wild plants, and for the most part on a relatively small scale, which in some cases is being reduced as the supply of available material decreases.

Distillation of the oils requires three principal pieces of apparatus —a boiler to generate steam, a retort where the plant material is subjected to the steam, and a condenser for the condensation of the steam and oil mixture. Receptacles are provided in which the condensed steam and the oil separate by gravity, after which the oil is purified by appropriate processes. Plant material which cannot be easily packed may first be crushed or chopped before it is loaded into the retort.

The bulletin also includes suggestions and drawings for the design and construction of volatile-oil stills in both experimental and commercial sizes.

ON THE STATE AND SPECIFIC HEAT OF GASES AT INFINITE VOLUME.

BY

R. D. KLEEMAN, B.A., D.Sc.

§ 1. *Matter is in the Atomic State when the Density is Infinitely Small.*

A pure substance of molecules a_2 is in equilibrium with atoms a according to the mass action equation

$$KC_{a_2} = C_a^2, \tag{1}$$

where C_{a_2} denotes the concentration of the molecules a_2, and C_a the concentration of the atoms. Hence the smaller the concentrations the smaller the fraction C_{a_2} becomes in comparison with the fraction C_a. At infinite volume C_{a_2} is therefore zero, or the atoms are in the free state. In the case of complex molecules in equilibrium with molecules of the type a_2, b_2, $\cdots$, the uncombined molecules a_2, b_2, $\cdots$ will, according to the foregoing equation, decompose into atoms at infinite volume. The complex molecules will then be formed from free atoms according to a mass-action equation resembling equation (1). Hence the concentration of these molecules also will be zero, or all the atoms will be in the free state. This result may be obtained by another method which is instructive.

The thermodynamical quantity known as the maximum work A of a mass of matter has the property that if the volume v and the masses M_a, M_b, $\cdots$ of the constituents a, b, $\cdots$ are each increased n times, its value is increased n times. It will therefore have the functional form

$$\begin{aligned} A = {} & M_a\psi_a\left(T, \frac{M_a}{v}, \frac{M_a}{v}, \cdots\right) \\ & + M_b\psi_b\left(T, \frac{M_a}{v}, \frac{M_b}{v}, \cdots\right) \\ & + M_a\phi_a(T) + M_b\phi_b(T) + \cdots, \end{aligned} \tag{2}$$

where T denotes the absolute temperature. At infinite volume the maximum work has a value obtained by writing $v = \infty$ in the foregoing equation. The value of the maximum work of the isolated constituent a is obtained by writing $v = \infty$ and $M_b = 0$, $M_c = 0$, $\cdots$, and so on for the other constituents. The values of the functions ψ_a, ψ_b, $\cdots$ are evidently the same in each case, and the maximum work of the substance is therefore an additive property of its constituents. This signifies that no external work would be done on mixing the constituents at infinite volume, or the number of molecules would not be changed. Similarly it can be shown on obtaining an equation for the internal energy similar to (2) that no change in internal energy takes place on mixing. Hence the nature of the molecules, besides their number, remains unchanged on mixing. And since no combination takes place between different molecules, we would expect that this should also hold for the atoms of a pure substance.

§ 2. *The Specific Heat of Atoms at Infinitely Small Concentrations as affected by the Heat of Evaporation being Zero at* $T = 0$.

The writer [1] has shown that the adiabatic of zero entropy corresponds to $T = 0$, or to zero temperature. Hence

$$\frac{L + \omega}{T} = 0 \tag{3}$$

at $T = 0$, where L denotes the internal heat of evaporation, and ω the external work done during evaporation. Since $T = 0$ and $\omega = RT$, it follows that

$$L = 0. \tag{4}$$

Another proof of this remarkable result may be based on Clapeyron's equation

$$L = \left(T\frac{dp}{dT} - p \right)(v_2 - v_1), \tag{5}$$

[1] *J. Phys. Chem.*, 31, 940 (1927).

where v_2 and v_1 denote the volumes of the vapor and the condensed phase respectively at the pressure p and temperature T. The equation may be written

$$p(v_2 - v_1) = L\frac{p}{T\frac{dp}{dT} - p}. \qquad (6)$$

The factor of L is indeterminate in form at the absolute zero of temperature, since $p = 0$ and $T = 0$. Its value may be obtained by successive differentiations of numerator and denominator, or we may suppose that near $T = 0$ we have $p = aT^n$, which gives a finite value for the factor. Therefore since $p(v_2 - v_1) = RT = 0$, we have $L = 0$. This result will be used presently.

It is of importance and interest to notice that the alternate way of obtaining $L = 0$ corresponds to establishing in an entirely different way the result quoted that the adiabatic of zero entropy corresponds to $T = 0$. It can then easily be further shown that the zero of internal energy must lie on this adiabatic, and that it corresponds to the substance being in the condensed state under the pressure of its vapor, a result established in a previous paper.[2]

We will now pass a substance initially at $T = 0$ under the pressure of its vapor, which is zero, through the following cycle, and equate to zero the change in internal energy: Thus let us: (*a*) evaporate the substance giving rise to an increase in internal energy equal to L, which is zero (Equation (4)); (*b*) raise the temperature of the vapor to T_m, at which the internal heat of evaporation begins to be finite and has the value L_m. The increase in internal energy is $C_\infty T_m$, where C_∞ denotes the average specific heat of the vapor between 0 and T_m; (*c*) condense the vapor, which gives rise to an increase in internal energy equal to $-L_m$; (*d*) lower the temperature of the substance in contact with its vapor to zero. This gives rise to an increase in internal energy equal to $-CT_m$, where C denotes the average internal specific heat of the condensed substance between 0 and T_m.

[2] *J. Phys. Chem.*, **31**, 747–756 (1927).

On equating the change in internal energy to zero, and remembering that $L = 0$, we obtain

$$T_m C_\infty - L_m - T_m C = 0. \tag{7}$$

Now T_m at the most has a value of several degrees (see (*b*)), L_m is of the order of several thousand calories per mol; therefore if C is normal, the internal specific heat C_∞ of the vapor has an average value of several hundred calories over the range of temperature from 0 to T_m. Specific heat measurements so far have not yet brought to light any abnormally large values of C for substances, and C_∞ has therefore in most cases abnormally large values near the absolute zero of temperature.

§ 3. *The Specific Heat of Atoms at Infinitely Small Concentrations as affected by the Instability of the Condensed State at or near the Absolute Zero of Temperature.*

Suppose that a substance in the condensed state has its temperature decreased to the absolute zero of temperature, and that the amount of heat given out during the process is *not* equal to the controllable internal energy. In that case the substance will finally not be under zero pressure of its vapor, since that state [2] corresponds to the zero of internal energy. The pressure will therefore not be zero, but might be quite large. On, however, allowing the substance to expand adiabatically and doing external work, its internal energy would be further reduced, and would finally be zero, which state would correspond to the substance being under zero vapor pressure. No change in temperature would take place during the expansion since we have seen in § 2 that the adiabatic of zero entropy corresponds to $T = 0$. Hence if the thermodynamical equation

$$\frac{\partial u}{\partial v} = T \frac{\partial p}{\partial T} - p, \tag{8}$$

where u denotes the internal energy at the volume v, pressure p, and temperature T, is applied to this expansion, we obtain

$$\partial u = - p \cdot \partial v, \tag{9}$$

since $T = 0$, or the decrease in internal energy is completely transformed into external work. The writer has already shown [3] that white tin behaves in this manner. We will see presently that there are besides other substances belonging to this class.

Let us carry out a cyclic process in this connection. Suppose that on lowering the temperature of the condensed substance it becomes unstable before zero temperature is reached at the temperature T_u. Now let us: (*a*) apply a pressure to the substance to keep its volume constant, and lower its temperature to zero. The increase in internal energy is equal to $-T_uC_v$, where C_v denotes the average internal specific heat of the condensed substance between 0 and T_u; (*b*) allow the substance, which is at $T = 0$, to expand adiabatically till its pressure is zero. Let $-u$ denote the increase in internal energy; (*c*) allow the substance to evaporate. The internal heat of evaporation is zero since $T = 0$; (*d*) increase the temperature of the saturated vapor to T_u. The increase in internal energy is equal to T_uC_∞, where C_∞ denotes the average internal specific heat of the vapor between 0 and T_u; (*e*) condense the vapor, which gives rise to an increase in internal energy equal to $-L_u$, where L_u denotes the internal heat of evaporation at the temperature T_u.

On equating the change in internal energy to zero we obtain

$$-T_uC_v - u + T_uC_\infty - L_u = 0$$

or

$$C_\infty = \frac{L_u + u}{T_u} + C_v. \qquad (10)$$

If T_u is zero, L_u is zero, and since u is finite, u/T_u is infinite under these conditions. But this is inadmissible, and hence T_u, the temperature at which instability begins, cannot be zero. In other words, if a substance is liable to become unstable and develop a high pressure on sufficiently lowering the temperature, this will take place at a temperature which

[3] *J. Phys. Chem.*, 31, 1669–1673 (1927).

is always above zero. Hence, since L_u amounts to several thousand calories per mol, and the value of u is unrestricted, the value of the right-hand side of the equation may amount to hundreds of calories, since T_u in most cases is not likely to be very large. The specific heat of the vapor of the substance would, under these conditions, be abnormally large over a region of temperatures adjacent to the absolute zero.

We have already seen that white tin belongs to this class of substances.[3] A few others will now be considered. The heats of formation, or the heats given out by substances in being formed from their elements, for the substances H_2O, CH_4 and NH_3 per mol in the gaseous state at room temperature are about 57,880, 18,300, and 9,500 cals. respectively. The heat is derived from the internal energies of the elements, and therefore, for example, the sum of the internal energies of the elements of a mol of H_2O is larger than 57,880 cals. Now the writer has calculated the internal energies of mols of H_2, C, O_2 and N_2 under the pressure of one atmos. at 298° K. from the data used by G. N. Lewis [4] for calculating the entropies, and obtained the values 1,100, 45, 2,980, and 3,090 calories respectively. But according to the above heats of formation these internal energies are very much too small. We conclude therefore that these substances become unstable in the condensed state at certain temperatures (probably quite near to $T = 0$), and if cooled to zero at constant volume will then have to be allowed to expand before their zeros of internal energy are reached. The change in internal energy $-u$ that takes place during the latter process in these cases will evidently be quite large, i.e., of the order of thousands of calories. Therefore the specific heat of these substances at infinitely small concentrations will be abnormally large near the absolute zero of temperature.

§ 4. *The Specific Heat of Atoms at Infinitely Small Concentrations as affected by their Forming Molecules at Finite Concentrations.*

In a previous paper [2] the writer has shown that the

[4] *J. Am. Chem. Soc.*, **39**, 2554 (1917); **44**, 1008 (1922).

controllable internal energy of a substance is zero when it is in the condensed state under its vapor pressure at the absolute zero of temperature. Since we have just seen that the internal heat of evaporation is zero at $T = 0$ (§ 2), it follows that the internal energy of the vapor is also zero at $T = 0$. The internal energy u_∞ of a substance at infinite volume at the temperature T may therefore be written

$$u_\infty = TC_\infty, \tag{11}$$

where C_∞ denotes the average specific heat at constant volume between the temperatures 0 and T. Now suppose that the substance, which is in the atomic state since its volume is infinitely large (§ 1), is compressed at the constant temperature T till its volume is finite and that the atoms now form molecules with a decrease in internal energy equal to Δu. This decrease in energy takes place at the expense of the internal energy of the substance in the atomic state. Hence by the help of equation (11) we have

$$\Delta u < TC_\infty.$$

An interesting case in this connection is hydrogen. At a temperature of 300° K. a mol. of hydrogen at a finite volume, we know, consists of molecules H_2. The heat of formation of a mol. of H_2 from its atoms, or the heat evolved, is equal to about 80,000 cals. This is equal to the value of Δu in the foregoing inequality, and since $T = 300$, the average value of the specific heat of atomic hydrogen at infinitely small concentration between 0 and 300° K. is greater than 266 cals. Actually it will be much greater at certain temperatures.

We thus have three effects which are responsible for the vapor of a substance at infinite volume possessing abnormally large values of the specific heat, especially near the absolute zero of temperature. The effect described in § 2 occurs with every substance; the effect described in § 3 occurs only with substances that become unstable and exert a considerable pressure at a certain temperature; and the effect described in this Section occurs only with atoms that may form compounds with a considerable evolution of heat.

§ 5. *Changes Associated with Abnormally Large Values of the Specific Heat.*

If a substance at constant infinite volume has a specific heat of about a thousand calories, as we have seen may easily happen, this must be associated with very pronounced changes in the electronic configuration of the atoms with change of temperature. These changes may conceivably be associated with very pronounced changes in the physical and chemical properties of the atoms. They may also be associated with the emission of electromagnetic radiations since in the rearrangement of the electrons some must fall through very high potentials. It is not improbable that the cosmic radiation, which in this country has been exhaustedly studied by Millikan [5] and his associates, and which has a penetrating power considerably greater than that of the γ rays of radium, is of this origin. The interstellar space must contain atoms of H, O, N, etc., whose temperature is probably very low, and whose further decrease might give rise to the radiation in question. Since the upper layer of the atmosphere must consist of matter in the atomic state at a low temperature, this would be a special source of the radiation. If the greater part of the radiation came from this layer, it can easily be shown that the radiation coming in horizontally to the Earth's surface is more intense for a given solid angle than that coming in vertically. It would be of great interest and importance if experiments were carried out to test this.

SCHENECTADY, N. Y.

[5] *Phys. Rev.*, **28**, 851 (1926).

A CAPACITY MEASUREMENT METHOD.

BY

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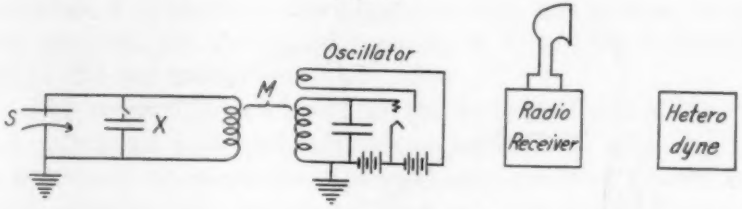
Engineer, Radio Corporation of America.

LET S of Fig. 1 be a calibrated condenser and X an unknown capacity (less than the maximum value of S). The oscillator is constructed with suitable precautions to insure a reasonable constancy of frequency and is built to oscillate at say 608 kilocycles. The coil connected to S is of as low

FIG. 1.



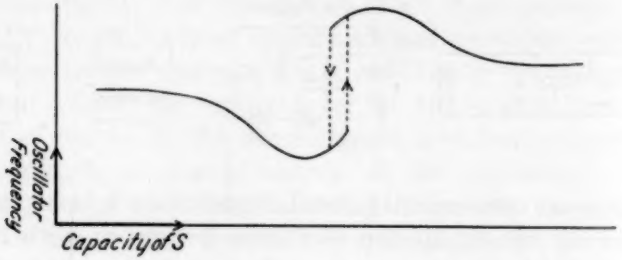
resistance as conveniently possible and of such inductance as to tune its circuit to the oscillator frequency with X disconnected at its live terminal and S somewhere near maximum. The heterodyne is adjusted to give any desired beat frequency in the output of a radio receiver located in the vicinity.

It is easy to obtain, inside of a few moments' juggling with the value of the mutual inductance M and the amount of feed back in the oscillator circuit, a condition where the following occurs: as S is increased a point is passed where the beat note changes discontinuously to a different pitch. If S is then decreased, the discontinuity in pitch reoccurs, this time at a value of capacity S slightly smaller than before. By careful adjustment of M these two critical values of S can easily be brought within a half of one micromicrofarad of each other. From now on no further adjustment need be made of

the apparatus, and the value of capacity X is determined as follows: with X disconnected note critical capacities of S. Then with X connected note the critical capacities of S. The capacity of X is the difference between the mean of the first pair of critical capacities and the mean of the second pair. (Unless the utmost precision is sought it would be enough to use only one of the pair of critical values, say the greater value, in each case. It is obviously necessary to avoid any change in wiring or other stray capacities when X is connected.)

The advantages of this method are: first, its accuracy, as the critical value can be read to less than a tenth of one micromicrofarad reproducibly. Secondly, the ease of finding the critical capacities, as the frequency jump occurs exactly

FIG. 2.



at one setting and only at that setting. And thirdly, the simplicity of the apparatus, as excellent results can be had with the simple oscillator arrangement of Fig. 1 while the heterodyne can be dispensed with entirely by using the carrier of some broadcast station and adjusting the oscillator to form beats.[1] Incidentally it makes no difference to the results if the heterodyne frequency is not constant.

By observing the variation of the beat note (when the heterodyne frequency is adjusted considerably below the oscillator frequency) it will be found that the effect upon

[1] If possible, however, it is much preferable to work with lower frequencies throughout, say about 50,000 cycles, in order to minimize the effects of the unavoidable inductance of the wires connecting S to X.

oscillator frequency produced by varying S is qualitatively as shown in Fig. 2. This could have been predicted by considering the variation of effective reactance of the oscillator coil caused by its coupling to the circuit containing S, together with the possible oscillation frequencies in coupled circuits.

The method has been found useful in calibrating variable condensers. In this case it is only necessary to disconnect the condenser once in a while to make sure the critical values of S with the condenser disconnected have not changed due to a slow drift in oscillator frequency. It is also possible to calibrate condensers whose capacity exceeds that of S by starting with another capacity in parallel with S (or an inductance in series with the coupling coil) and taking it out when S cannot be reduced any further, and getting, from this point on, not the actual capacity of X, but the increases above the last measured actual value.

This method, which I will call the method of discontinuity (as contrasted with null methods or methods of adjusting to a maximum or minimum of something), could obviously be used equally well for comparison of inductances with a calibrated standard, and probably in many other cases where an indication of resonance is required.

Fog-Dispelling Methods Too Costly for Commercial Use. (U. S. Department of Agriculture, Clip Sheet, No. 510.) Attempts to dispel fog by artificial means have not proved successful, says the Weather Bureau. Many different schemes have been advanced, but the places that have always been notorious for fogs still have them. Years ago Sir Oliver Lodge thought he had solved the problem by installing an electric contrivance on his house in Liverpool, but the city on the Mersey is still afflicted with fogs. The London County Council was approached with a scheme for clearing away the celebrated London fogs by the use of explosives. As a similar scheme had been tried without result in Italy for dispelling hailstorms, the county authorities declined to provide funds for this experiment.

Shortly before the World War the city of Lyons voted money for experiments in preventing the formation of fog in that city by coating the rivers Rhone and Saone with oil. About the same time the Cottrell process of electrical precipitation, which is successfully applied in treating industrial dusts and fumes, was tried on the fogs of the California coast, but nothing seems to have resulted. Quite recently the naval aircraft factory at Philadelphia has been the scene of experiments in dissipating fog by means of electrified sprays. No tangible results have been announced. Schemes for draining off fog-laden air from flying fields and also for warming the air over such places and thus causing the fog to evaporate have been investigated and found impracticable.

On a small scale and in favorable circumstances fog can be dispelled but all known methods are too costly for commercial use, and so could not be applied on the vast scale on which many fogs occur, even were they of proved use.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

RADIO AIDS TO CIVIL AIRWAYS.

THE bureau has now in operation two experimental radio stations for aeronautic work carrying on active development work on aids to air navigation. These two stations are located at College Park, Md., a suburb of Washington, D. C., and Bellefonte, Pa., which is located on the transcontinental airway midway between New York and Cleveland. The services of both stations are available to all aircraft able to make use of them.

At College Park there is a directive radio beacon which has heretofore been equipped to send signals of the aural interlocking variety. Recently this beacon has been rebuilt to send in addition signals modulated at two low frequencies necessary for the visual indicator system that the bureau has recently developed. The College Park station is equipped with other special types of equipment for the sending of signals for experimental purposes. At Bellefonte the directive radio beacon is being remodeled so that it can send signals for use of the visual system in addition to the aural system. By May 15 three airplanes of the National Air Transport, Inc., using the Bellefonte station, and three airplanes of the Pitcairn Aviation, Inc., using the College Park station, will be equipped with suitable radio receiving sets, including visual indicators, so that practical flying tests by these air mail contractors may be carried out. Much valuable information is expected to result following the inauguration of these service flights.

The College Park station is also equipped to transmit telephone or telegraph messages to airplanes. This station, which is remotely controlled from the field, is available for experimental work through the courtesy of the American

* Communicated by the Director.

Telephone and Telegraph Company. The Bellefonte station is also provided with a remotely controlled 1-kw. set whereby telephone or telegraph messages can be sent to airplanes in flight. The practical operation of the handling of weather broadcasts to aircraft in flight by radio telephony is to be included in the service flights mentioned, using these two stations.

The beacons operate in the frequency band 285 to 315 kc., and the telephone stations in the band 315 to 350 kc. These are allocated to air service by the 1927 International Radio Convention. For the present the beacons are adjusted to the frequency of 290 kc., and the telephone stations to 333 kc.

The directive radio beacon is a special kind of radio station, usually located at an airport, just off the landing field. Instead of having a single antenna like an ordinary radio station, it has two loop antennas at an angle with each other. Each of these emits a set of waves which is directive, i.e., it is stronger in one direction than others. When an airplane flies along the line exactly equidistant from the two beams of radio waves, it receives signals of equal intensity from the two. If the airplane gets off this line, it receives a stronger signal from one than the other.

The indicator connected to the receiving set on the airplane shows when the signals from the two beams are received with equal intensity, by means of two vibrating reeds which are tuned to different modulating frequencies used on the two antennas at the directive radio beacon station. When the beacon signal is received, the two reeds vibrate. The tips of these reeds are white in a dark background, so that when vibrating they appear as a vertical white line. The reed on the pilot's right is tuned to a frequency of 65 cycles and the one on the left to 85 cycles. It is only necessary for the pilot to watch the two white lines produced by the vibrating reeds. If they are equal in length, he is on his correct course. If the one on his right becomes longer than the other, the airplane has drifted off the course to the right (into the region where there is more of the 65 cycles). If he drifts off the course to the left, the white line on the left becomes longer.

The visual indicator system comprises a small indicator unit and a receiving set weighing between twelve and sixteen pounds with batteries weighing an additional sixteen pounds. Very successful flights have been made up to 135 miles. To a large extent the device is little affected by interference. It is only partially affected by airplane engine ignition interference. Such interference does not change the operating characteristic of the indicator signal, but merely reduces the distance range from the beacon station. The system was recently demonstrated to representatives of the various Government departments.

During the latter part of 1927 several flights were made from Bellefonte in order to test the reliability of the directive type of beacon. There were both day and night flights. It was found that at night up to fifty miles from the beacon the directions were reliable, between 50 and 75 miles they were usually accurate but uncertain at times, from 75 to 100 they were frequently unreliable, and beyond 100 miles the beacon could not be used. No such discrepancies were found during daylight hours. Two solutions are under investigation. Placing the beacons closer together and using a vertical antenna on the aircraft are expected to assist greatly. The greatest use of the beacon is within 30 miles of the field where it is always reliable. A paper describing these night effects in detail will be published in an early issue of the *Proceedings of the Institute of Radio Engineers.*

Special receiving sets and antennas for use on airplanes in connection with the beacon system have been developed. They are even simpler than those in use hitherto. The familiar trailing wire, with its possible dangers and its directive effect introducing apparent variation of the course, is eliminated. It is replaced by a short vertical metal rod. The use of this improved antenna is made possible by a special receiving set which is highly sensitive, light in weight, and exceptionally proof against the engine ignition interference. This receiving set and antenna system can be used to receive telegraphy, telephony, aural interlocking beacon signals, or

to operate the visual indicator mentioned. The visual indicator plugs into the set in place of headphones. No other change is required.

While there are no commercial receiving sets at present available which are suitable for use on aircraft at the new frequencies for the air services, close coöperation is being maintained between the bureau and several commercial companies working on various problems related to radio aids for air navigation. It appears that suitable receiving sets and auxiliaries will soon be offered on the market. Publications describing the bureau's work on radio aids to air navigation in detail are in preparation. Announcement will be made in this bulletin when this material is available.

CALCULATION OF ANTENNA CAPACITY.

A PAPER just issued by the bureau gives a discussion of methods and formulas for the calculation of the capacity of various common types of antennas. In the past, two different basic methods have been used for such calculations, but the two methods have not always given the same result. The present paper shows that results of calculations by the two methods agree if appropriate formulas are used. One method however is the more general and useful. A set of working formulas for calculating the capacity of the more common types of antennas is developed. Tables of constants for facilitating numerical calculations are given, together with tables for the capacity of single-wire horizontal and vertical antennas and two-wire antennas. This paper, Bureau of Standards Scientific Paper No. 568, "Methods, Formulas and Tables for the Calculation of Antenna Capacity," by F. W. Grover, may be obtained for 20 cents from the Superintendent of Documents, Government Printing Office, Washington, D. C.

CRITERIA OF GASOLINE VOLATILITY.

IN the early days of the petroleum industry when most of the gasoline came from the Pennsylvania fields, it was tested

and sold largely on the basis of gravity, and high Baumé gravity (high test) was a general indication of high volatility. But with the discovery and development of oil fields in other parts of the country gravity gradually lost its significance, for a gasoline from a California crude, for example, might have a considerably lower gravity (A. P. I.) than one from a Pennsylvania crude and yet the former might be more volatile. The increasing use of cracked and of blended gasolines in recent years has removed any remaining significance which gravity had as an indication of volatility, although a large amount of gasoline is still sold to the public on this basis.

Six years ago the Federal Government adopted specifications for gasoline which were based on the distillation test of the American Society for Testing Materials and not on gravity. This test gives an A. S. T. M. curve showing the temperatures at which various percentages of the gasoline are evaporated according to a definite procedure. These temperatures are however much higher than those necessary to vaporize the same gasoline in such air-gasoline mixtures as are supplied by the carburetor of an automobile engine. In order to study the volatility of gasoline under conditions more like those in the engine manifold, an equilibrium air-distillation apparatus was designed at the Bureau of Standards which gives curves indicating the temperatures at which various percentages of the fuel are evaporated under approximate manifold conditions.

Last year, on the basis of data for 9 gasolines, it was reported in *Technical News Bulletin* No. 119 (March, 1927) that at 5 per cent. and at 15 per cent. evaporated the absolute temperatures on the A. S. T. M. and equilibrium air-distillation curves are related to each other by means of simple ratios. Since that time, work on 25 gasolines has shown that similar ratios are obtainable at any percentage evaporated from 5 to 95 per cent. Thus, from the A. S. T. M. distillation test, which is in common use throughout the country, it is possible to compute volatility curves in terms of the mixture ratios used in the engine. A chart has been prepared for obtaining

volatility data graphically and a limited number of copies of this chart are available for distribution.

The general relations between the A. S. T. M. and equilibrium air-distillation curves do not hold at 100 per cent. evaporated for the reason that there is always a residue left in the A. S. T. M. test which is not evaporated, so that it is impossible to obtain the temperature of complete evaporation on the A. S. T. M. distillation curve. The temperature of complete evaporation on the equilibrium air-distillation curve can be obtained however and this temperature is called the dew point. On the basis of measurements with a large number of gasolines and with a variety of mixtures of air and fuel, a general relation was found between the dew point temperatures of these mixtures and the temperature at 90 per cent. evaporated on the A. S. T. M. distillation curve. This relation was checked by experimental work with a different type of apparatus which gave the dew point temperatures directly.

The temperature of complete evaporation is of considerable importance on account of its bearing on the problem of normal engine operation. For example, it is advantageous to have a fuel with sufficient volatility so that the air-fuel mixtures drawn into the cylinders will not contain enough unevaporated gasoline to cause serious dilution of the crankcase oil. It is also advantageous because it reduces the necessity of adding heat to the mixture by means of auxiliary manifold heaters. On the other hand, the use of a fuel with too high a volatility in an engine equipped with manifold heaters may result in superheating the mixture and thereby cause loss in power.

The temperature at which 90 per cent. of the gasoline is evaporated on the A. S. T. M. distillation curve is a real criterion of the volatility which is of interest under normal operating conditions. A gasoline with a low 90 per cent. point will evaporate more readily in the engine manifold, and a classification of gasolines on the basis of their 90 per cent. points would seem to be a logical step in the direction of giving the motorist real information about volatility. The

end point on the A. S. T. M. distillation curve is frequently used for this purpose but it is misleading as a criterion for complete volatility. Thus one gasoline may have a 450 end point and another a 400 end point and still both may have the same 90 per cent. point and hence would have the same volatility under normal operating conditions. On the other hand, two gasolines with different 90 per cent. points will differ as regards complete volatility even though both are "400 end point gasolines."

THERMAL CONDUCTIVITY STANDARDS.

A NUMBER of different laboratories in the United States and Canada are engaged in testing and investigational work in the field of thermal insulation at ordinary temperatures. Most of these laboratories use the so-called "hot plate" method of test, but at best it has been difficult to judge the agreement in results between the various laboratories, since the class of materials tested, i.e., insulating materials, are not particularly definite and reproducible, and in addition test conditions vary from place to place.

As part of a coöperative program with the Celotex Company, an attempt is being made to determine the accuracy which can be expected from the various devices now in use for measuring thermal conductivity. A number of test specimens have been prepared which may be termed "thermal conductivity standards," and these are being furnished to the various institutions possessing "hot plate" conductivity apparatus.

The test specimens consist of slabs of homogeneous cork composition material 8 or 12 inches square, to the surfaces of which thermocouples are permanently fastened, so that the boards are in reality "conductimeters" or "heat meters." A regular thermal conductivity measurement, consisting of independent measurements of heat flow, thickness, and temperature difference between hot and cold plates, is made on a pair of boards, and in addition readings are taken of the

thermocouples permanently fastened to the specimens. The last-named measurement gives a check on the accuracy of the heat flow measurement, independent of errors made in the measurement of thickness or temperature difference between the plates of the apparatus.

The standard specimens are coated with waterproof varnish, but this treatment does not protect against slow changes in moisture content with changes in atmospheric humidity. The specimens are therefore always dried in an oven before each determination.

The results thus far obtained from a few laboratories show rather good agreement with those obtained at the bureau. To expedite the survey, a new hot plate has been constructed for use primarily in standardization work. In the design of this plate, the aim has been to obtain the highest possible accuracy rather than to sacrifice in favor of simplicity of construction.

The bureau will be glad to furnish standard conductivity samples to any laboratory wishing to coöperate in this work.

FIRE RESISTANCE OF SAND-LIME AND CONCRETE BRICK WALLS.

A SERIES of fire tests of brick walls was completed recently at the Bureau of Standards. The object was to determine the fire protection, strength, and stability under fire conditions of this construction. An item giving the results for clay and shale brick walls was published in *Technical News Bulletin* No. 124 (August, 1927). The present item gives the results for sand-lime and concrete bricks.

Materials and Test Specimens.—Sand-lime and concrete bricks from two sources for each were included. The harder sand-lime brick would be graded as medium under present specifications of the American Society for Testing Materials, and the other as soft, mainly on the score of absorption, the compressive strength on edge ranging from 1690 to 4720 lbs./in.^{2}, and the modulus of rupture from 460 to 930 lbs./in.^{2}. The concrete bricks would pass the present A. S. T. M.

tentative specifications for concrete building bricks with some margin, the average compressive strength flatwise being 2780 and 2920 lbs./in.^{2} for bricks from the respective sources. The aggregate used for both the sand-lime and the concrete bricks was siliceous sand. The bricks were built into walls 16 feet long and 10 to 11 feet high for tests in the large furnace, and 4 feet wide and 4 feet high for tests in the small furnace, 8 tests being made with walls of each size. Sand-lime and concrete bricks also formed parts of six walls subjected to fire and water tests.

The walls were laid up with Portland cement-lime mortar consisting of 1 : $1\frac{1}{4}$: 6 volume parts of cement, hydrated lime, and dry sand, respectively, which was mixed with water to the consistency required by the masons. The bricks were laid flat as in common or running bond, with one full header course for every five stretcher courses. The greater number of walls tested in the large furnace were built by a masonry contractor who was awarded the work on the basis of competitive bids, and the workmanship was apparently barely up to the average in building construction. The other walls were built by masons in the employ of the bureau, and the grade of workmanship, as indicated by the way in which the joints were filled and pointed, was probably a little above the commercial average.

Method of Testing.—The walls were built into movable frames, and for the test were placed to form one wall of the furnace chamber. Some of the walls were built solidly into the frames, which were rigid enough to restrain the greater portion of the expansion of the wall during test, thus duplicating conditions where fire division walls are built between heavy floors and columns. Six walls were tested under a working load of 160 pounds per square inch of gross area, maintained constant during the fire test, to determine the adequacy in this particular. Other walls were built free from the containing frames at the sides and top, permitting free movement of the wall during test, which is representative of the unrestrained condition of walls in minor buildings, or

the top story of walls in higher buildings, where light, non-fire-resistive interior and roof construction does not appreciably restrain the wall at the floor and roof lines.

The furnace temperatures were controlled to conform with standard American fire-testing practice, the fire exposure being continued in the fire endurance tests until or past the time when certain given temperatures obtained on the unexposed side, unless failure under the applied load occurred earlier. In the fire and water tests the walls were exposed to fire for one hour, after which they were pulled away from the furnace and a hose stream from a $1\frac{1}{8}$-inch nozzle under a water pressure of 50 lbs./in.^{2} applied over the hot side.

Stability and Load-Carrying Ability.—The deflections of restrained and loaded walls were toward the fire and attained a maximum at the center of the wall. For 8-inch walls the maximum deflections of the large walls averaged 2 inches, and for the 12-inch walls, $1\frac{1}{4}$ inches, at from 2 to 6 hours after the start of the test. For the unrestrained walls the maximum deflections took place at the top of the wall and were away from the fire, the average of maximums obtaining at the end of 6 hours, being $9\frac{1}{4}$ inches for 8-inch walls. The recovery from deflections on cooling ranged from one-fourth of the maximums obtaining during test to full recovery.

No 8-inch walls failed because of excessive deflection or under the applied working loads. One 12-inch wall of soft sand-lime bricks failed under the working load at a little before 10 hours after the start of the test through weakening of the brick on the fire side. It is probable that few fire conditions in buildings will give rise to fires as severe as 10 hours of the standard fire test.

Fire Effects on Brick and Masonry.—For the restrained walls, cracks on the side away from the fire of over $\frac{1}{16}$ inch in width were rare. For the unrestrained walls cracks up to $\frac{5}{8}$ inch were formed in 8-inch walls toward the end of the test, these being narrower or closed on the fire side. The headers were seldom found cracked in the central portion of the wall, so that the integrity of the wall as a building member was maintained.

Serious damage to the bricks was confined to those next to the fire except for tests lasting over 6 hours. Cracks parallel with the face of the wall were formed in some of the bricks from $\frac{1}{2}$ to $1\frac{1}{2}$ inches from the fire side. Hard bricks were more susceptible to cracking than the softer bricks, although showing greater strength after the fire test. The full discussion of fire effects and possibility of re-use involves a greater amount of detail than can be given in the present item.

Fire Resistance Classifications.—According to present specifications for fire tests, the classification for load-bearing walls is based on ability to sustain the working load and to prevent temperature transmission through the wall to such an extent as to endanger combustible materials in contact with the unexposed side. The average temperature rise permitted is 139° C. (250° F.), or a maximum rise of 181° C. (325° F.) for any single point. The temperatures are measured under asbestos felt pads, 4/10 inch thick, placed against the unexposed side of the wall. The periods given in the table are determined by temperature transmission unless otherwise noted. The limit for the 12-inch walls is determined by load-carrying ability for walls made from some of the bricks. The periods given are within the lower range of values obtaining in the fire endurance tests.

The factor of safety that should be applied to these fire-resistance periods depends on the variation in material and workmanship to be expected in building construction beyond that present in the tests. The drier condition of party and fire walls after years of service in the interior of heated buildings, as compared with that of the walls tested, and the increase in temperature on the unexposed side after the prescribed temperature limit was reached and the fire shut off would of course influence the choice. Some information on the extent of these effects was developed in the tests. The use of factors of safety of $1\frac{1}{4}$ to $1\frac{1}{2}$ on the results of fire endurance tests has been advocated. Insofar as it concerns the constructions tested, the higher value does not appear to give

a greater margin than necessary. On this basis a wall giving an ultimate fire resistance of 3 hours can be applied as protection against a fire condition equivalent to not more than 2 hours of the standard test, and a wall of 9 hours test rating to a fire condition estimated as not more severe than 6 hours of the test furnace exposure.

The fire and water tests developed nothing that would change the conclusions based on the fire endurance tests.

Ultimate Fire Resistance Periods of Solid Concrete and Sand-Lime Brick Walls.

Kind of Brick.	Nominal Thickness.	Building Members Projecting into Wall.	Fire Resistance Period.
Concrete	8-inch unplastered	None or incombustible	6½ hours
ditto	ditto	Combustible	3
ditto	12-inch unplastered	None or incombustible	15
ditto	ditto	Combustible	12½
Sand-lime	8-inch unplastered	None or incombustible	8
ditto	ditto	Combustible	3½
ditto	12-inch unplastered	None or incombustible	[1]10 [2]15
ditto	ditto	Combustible	[1]10 [2]13

The periods apply for both bearing and non-bearing walls unless otherwise indicated. Those marked with a note [2] are only to be used for non-load-bearing walls when the probable exposure approaches the period given in the table. However, such walls are safe for bearing purposes for lower periods. For bricks laid flatwise and for periods not exceeding 6 hours, either Portland cement, cement-lime, or lime mortar of volume proportions not leaner than 1 : 3, cement or lime, and sand, respectively, can be used. For walls having periods of over 6 hours, Portland cement or cement-lime mortar should be used.

When combustible floor members enter into solid walls, the periods are premised on the assumption that they project not more than 4 inches into the wall, and, where entering from both sides, that they are so placed and protected as to have not less than 4 inches of solid masonry between them.

[1] Determined by load-carrying ability.

[2] Determined by temperature transmission only and obtained by comparison with results of tests of concrete brick walls.

THERMAL EXPANSION OF FIRE-CLAYS.

The study of the fundamental qualities of representative fire-clay refractories and individual clays was described in *Technical News Bulletin* No. 125 (September, 1927).

The linear thermal expansion has been observed from room temperature to 900° C. by means of the interferometer on a total of 25 clays burned at 1400° C. for five hours. These are the clays used in the manufacture of the 17 brands of fire-brick included in this investigation. The clays may be classified according to the thermal expansion into four groups as follows:

1. Eleven have a rapid rate below 200° C., due to the presence of tridymite and cristobalite, and a uniform rate from 200 to 900° C.

2. Three have rapid rates of expansion below 200° C. and at approximately 600° C., due to presence of the different types of silica.

3. Nine have a uniform rate from room temperature to 900° C.

4. Two have a uniform rate from room temperature to approximately 725° C., at which temperature the rate increased until 850° C. was reached, after which it decreased.

In comparing these data with those obtained on the brick in which the clays were used either singly or blended and which were previously reported, it was noted that:

1. In four instances the rapid rate of expansion below 200° C. shown by the clays was not apparent in the bricks. It is possible that this difference is due to the blending of two or more clays which is favorable to the growth of mullite crystals at 1400° C.

2. Two brands of fire-bricks show a rapid rate of expansion at 600° C., which is not present in the individual clays. This expansion in the bricks is undoubtedly due to the nature of the grog added in the manufacturing process.

3. In two cases where bricks are manufactured from the same clay by both the stiff mud and dry press methods the expansion of the clay is higher than that observed on the brick of either type.

WORKABILITY OF PORTLAND CEMENT PASTES.

THE study of workability of Portland cement pastes has now included tests of three devices—the extrusion cylinder, the ball plasticimeter, and the capillary tube. The first device consists of a cylinder from which a piston forces the cement paste through an orifice, the piston moving at a constant speed.

The three methods have shown differences, in some cases very marked, in the behavior of various cements when tested in the form of neat cement pastes. Moreover, the relative order of the results is different for each of the three devices. It is apparent that this investigation must be continued to determine the extent to which the test method used influences the results obtained. Without this information no satisfactory comparison can be made of the relative workability of mortars and concretes prepared from these cements. It seems probable that the manner in which a cement is to be used should largely influence the choice of the method by which its workability is determined.

It is interesting to note that the ball plasticimeter and the capillary tube have both placed at opposite extremes of the groups of curves two cements submitted by one manufacturer. One of these cements was considered by the maker as highly plastic when used in concrete and mortars, while the other cement was thought to be of a decidedly opposite character.

CONTROL OF CLAY SLIPS BY USE OF ELECTROLYTES.

A STUDY is being made of protective colloid action in the casting of clay slips at the Columbus branch of the bureau. Tannic acid and peat have been used to date. The addition of small amounts of tannic acid or peat to slips containing little or no carbonaceous matter has been found to decrease the amount of water necessary to make up the slips and to increase markedly the cross-breaking strength of inch-bars from such slips. The composition of a typical body containing no organic matter is the following:

Tennessee ball clay No. 7	100	grams
Georgia china clay No. 4	400	do.
Flint	300	do.
Feldspar	200	do.
Sodium carbonate	1.25	do.
Sodium silicate	1.25	do.

The addition of 0.2 per cent. carbon in the form of tannic acid or peat (calculated as per cent. of dry weight of body before the addition of water) was found to increase the cross-breaking strength of inch-bars cast from such slips about 125 per cent., and to decrease by 20–25 per cent. the amount of water necessary to make up the slips. The addition of 0.05 per cent. carbon in the form of peat or tannic acid gave approximately the same cross-breaking strength as the larger (0.2 per cent.), but gave lower water economy. The addition of peat or tannic acid in concentrations considerably greater than 0.2 per cent. decreased the rate of setting of the slips. The aim in adding protective colloid evidently should be to select such a concentration of protective colloid as will give a large cross-breaking strength of bars and maximum water economy, without abnormally increasing the time of setting. The lower concentrations of peat and tannic acid (0.05 per cent. and 0.2 per cent.) do not decrease the rate of setting of the slip. It is also possible that the addition of protective colloid will aid in preventing the "livering" of slips which have stood for some time.

At the present time, the effect of tannic acid and peat is being tested, using only china clay, flint and feldspar as the body. Both English and Georgia china clays are being used.

"TRUE" SPECIFIC GRAVITY OF FELDSPARS.

Technical News Bulletin No. 129 (January, 1928) contained a report of the study of the thermal expansion of the 19 commercial feldspars under investigation. The following report summarizes the study of the true specific gravity of the raw, partially fused, and fused feldspars. A Hubbard type pycnometer, closed with a polished glass disk to seal the

capillary and prevent evaporation, was used in this study. Samples weighing approximately 5 grams were used. The weighings were made on a chemical balance sensitive to the fourth decimal. The pycnometer was dried at 110° C., the sample introduced, weighed and evacuated under a bell jar. Freshly boiled distilled water sufficient to cover the sample was then added through a separatory funnel. Then the pycnometer was removed, more water added, the sample allowed to settle and cooled to 20° C. ± 0.1° in a constant temperature water bath. After the sample had settled and cooled, the pycnometer was completely filled with water, wiped dry with a soft clean cloth and weighed.

The results shown in the following table indicate that the average values for the raw feldspars vary from 2.615 for sample No. 1 (high soda feldspar) to 2.574 for sample No. 19 (high potash feldspar). These values compare favorably with those found by other investigators. Since there is a difference of only 2 per cent. between the greatest and least specific gravities of the 19 feldspars, covering the field from albite to microcline, it is doubtful whether the determination of specific gravity will have any value as a practical test to determine the type of feldspar purchased.

For the determinations of the true specific gravity of the partially fused and fused feldspars the samples were pressed in mullite crucibles fired to cones 4, 8, 10, 12, 13, and 14, drawn at the desired temperature, and quenched in running water. The specimens were broken away from the crucibles, crushed between hardened steel surfaces, ground in an agate mortar, magnetic particles removed, passed through a No. 100 sieve, and the specific gravity determined.

The results show that the specific gravity of the feldspar decreases when fired to cone 4 and drops still more when fired to cone 8. When fired to cones 10, 12, 13, and 14 only slight differences are shown, indicating that the crystalline form has been nearly all converted to amorphous glass. The definite molecular structure of the feldspar crystal is evidently converted to leucite and glass on melting, as has been reported

by Morrey and Bowen,[1] and the glass resulting from undercooling shows a drop in specific gravity and an increase in volume. The average increase in volume for a feldspar fired to cone 4 is 4 per cent., fired to cone 8 is 7 per cent., and fired to cone 10 is 9 per cent. This conforms to data obtained by other investigators.

Feldspar Number.	True Specific Gravities of Feldspars in Terms of Equal Volumes of Water at 20° C.						
	Raw Feldspar.	Fired to					
		Cone 4.	Cone 8.	Cone 10.	Cone 12.	Cone 13.	Cone 14.
1	2.615	2.513	2.424	2.374			
2	2.613	2.517	2.422	2.407			
3	2.612	2.461	2.422	2.389			
4	2.614		2.428	2.420		2.413	
5	2.604		2.412	2.407		2.386	
6	2.602		2.454	2.422		2.393	
7	2.610		2.444	2.403		2.395	
8	2.595		2.404	2.397		2.388	
9	2.593		2.411	2.394		2.384	
10	2.598		2.412	2.402		2.400	
11	2.600		2.406	2.397		2.394	
12	2.598		2.403	2.408		2.377	
13	2.589		2.426	2.411	2.410		2.376
14	2.594		2.435	2.414	2.396		2.372
15	2.582		2.430	2.401	2.387		2.370
16	2.586			2.412	2.406		2.374
17	2.572			2.409	2.400		2.377
18	2.583			2.381	2.379		2.376
19	2.574			2.397	2.375		2.376

EFFECTS OF TEMPERATURE AND HUMIDITY DURING THE PREPARATION AND TESTING OF RUBBER COMPOUNDS.

THERE will soon be available a report by the physical testing committee of the rubber division of the American Chemical Society on the effects of temperature and humidity during the preparation and testing of rubber compounds. This report presents complete data and final conclusions based on an investigation conducted at the Bureau of Standards in accordance with a program drawn up by the physical testing committee. A comprehensive study was made with five cures of five typical compounds, involving several thou-

[1] "The Melting of Potash Feldspar," by G. W. Morrey and W. L. Bowen, *The American Journal of Science*, Vol. IV, July, 1922.

sand tests in which the humidity, temperature, and periods of exposure were varied both prior and subsequent to vulcanization. Photographs are included showing the apparatus used in conditioning the samples. Test methods are described in detail and the results are given in 52 tables and 98 charts. Data obtained show that previous to vulcanization relative humidity has a pronounced effect upon the stress-strain relation, while that of temperature within the range studied is practically negligible. Differences due to relative humidity vary both in degree and kind with the ingredients used. Length of exposure of compounds has an appreciable effect. Subsequent to vulcanization, relative humidity has but slight effect while that of temperature is pronounced. The effects due to temperature are not changed materially, in the compounds studied, by the compounding ingredients. Copies of this report will be available to those interested through the physical testing committee of the rubber division of the American Chemical Society and can be obtained when issued by addressing the chairman, Mr. J. E. Partentheimer, Fisk Rubber Company, Chicopee Falls, Mass.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

AN ELECTRICAL SOLUTION-MIXING DEVICE.[1]

By K. C. D. Hickman and D. Hyndman.

ELECTRICAL titration methods in general use employ electrodes immersed in the reacting liquids and give indications of hydrogen or other ion concentrations. The indications have been used by various workers to control automatically the mixing of the two reagents. Such electrical controls may be described as operating internally. The present method uses externally gaseous indicators such as sulfur dioxide or ammonia, which it detects by an 'electric nose' placed over the reacting vessel. The variations in current actuate a valve which limits the particular solution in excess at that moment. In this connection a special mechanism has been devised which requires so little energy for actuation that no amplification or relays are required on the electrical circuit for the 'nose' even though thousands of gallons of solution be handled each hour. The device is useful both in acidimetry and in oxidation—reduction reactions, particularly with complex mixtures, since only the chosen volatile constituent can affect the control.

VECTORIAL TREATMENT OF REFRACTION OF SKEW RAYS BY A PRISM.[2]

By L. Silberstein.

THE incident ray, of any orientation, being represented by the unit vector r, the refracted and ultimately emergent ray is expressed by the vector formula, $r' = r + g_1 n_1 + g_2 n_2$

* Communicated by the Director.

[1] Communication No. 321 from the Kodak Research Laboratories and published in *Ind. Eng. Chem.* 20: 213. 1928.

[2] Communication No. 333 from the Kodak Research Laboratories and published in *J. Opt. Soc. Amer.* 16: 88. 1928.

(given some time ago in "Simplified Method"), where n_1, n_2 are the normals of the two faces of the prism and g_1, g_2 are scalar factors; in obvious notation, $g_1 = \cos i_1 - \text{picos } i_1'$, etc. From this simple formula the two angular coördinates of the emergent in terms of those of the incident ray are now most directly deduced. If θ be the inclination of the incident ray to the edge of the prism and ϕ the angle between the first face of the prism and the plane through the edge parallel to the incident ray, then, for the emergent ray, $\theta' = \theta$, and, the scalar g_2 being readily eliminated,

$$\cos(\phi' - \epsilon) = \cos(\phi - \epsilon) - g_1 \sin \epsilon / \sin \theta,$$

where ϵ is the refracting angle of the prism. The factor g_1 is written explicitly in terms of incidence data. The advantages of the vectorial as compared with the usual treatment are brought out. The limiting condition, beyond which there is total reflection, is derived and discussed.

CONTRIBUTION TO THE THEORY OF PHOTOGRAPHIC EXPOSURE.[3]

By L. Silberstein.

IN the first part of the paper the original form of the quantum theory of photographic exposure and its several modifications are critically discussed. It is shown that none of them represents the photomicrographic findings with sufficient accuracy. The second and main part is devoted to nuclear theories, in which the element of chance is transferred from the impinging light to certain peculiarities of the grains themselves, viz., incipient nuclei haphazardly distributed among them. After a brief general introduction to such theories, a mathematical formulation of Toy's more or less qualitative theory is given. This is shown to lead to a formula which again deviates essentially from observed facts. Such being the case, an alternative type of nuclear theory of

[3] Communication No. 336 from the Kodak Research Laboratories and published in *Phil. Mag.* **5**: 464. 1928.

exposure is next considered in which the growth of the nuclei is explicitly taken into account. This was qualitatively suggested by Sheppard, Trivelli, and Loveland in their "Concentration Speck Theory." The ratio of growth of the nuclei in presence of light being assumed proportional to their instantaneous size, and the sizes of the pre-exposure nuclei being attributed a normal distribution frequency among the grains, the proportionate number, k/N, of grains affected by an exposure E is expressed by the formula,

$$k/N = \frac{\phi(g - \alpha) - \phi(ge^{-cE} - \alpha)}{\phi(g - \alpha) + \phi(\alpha)},$$

where ϕ stands for the error-function and g, α, c are constants. This is tested experimentally and shown to represent the majority of available data fairly accurately. In the closing section a refinement of this formula is considered, the effect of the finite size of, and the competition between, the nuclei placed upon the same grain being taken into account.

International Peat Congress to be held at Laon (Aisne), France, July 8 to 12, 1928. The labors of the First Congress of Peat, which was held from the 22d to the 25th of September, 1927, at Notre-Dame-de-Liesse near Laon (Aisne) proved that peat is a product capable of bringing not alone to France but to every country a source of additional wealth. The members of the Congress of 1927 on adjourning resolved to invite in 1928 all nations to participate in the 2d Congress, thus making it of an international character. Foreign delegates are invited to visit Laon to observe what has been achieved in French technique and at the same time to make their own contribution to the promotion of this valuable natural product. The activities of the congress will include the reading and discussion of communications, an exposition of machinery of extraction, treatment and utilization of peat, of verified investigations, and a convention of peat workers.

Those interested are requested to communicate with Secrétariat du Congrès International de la Tourbe, Office National des Combustibles Liquides, 85, Boulevard du Montparnasse, Paris (6e).

L. E. P.

NOTES FROM U. S. BUREAU OF MINES.*

EXPERIMENTS IN UNDERGROUND COMMUNICATION THROUGH EARTH STRATA.

MINE disasters occur rather frequently, and at such times communication is vital. In coal mines disasters are caused by explosions and fires and sometimes by large falls, cave-ins, or floods. Some explosions in coal mines are so violent and extensive that they kill outright or almost immediately suffocate every man underground. However, only a few men in the actual zone of the explosion are ordinarily killed outright; unless the others are in atmospheres containing the deadly afterdamp (carbon monoxide), which is always present after an explosion, they may be rescued later, sometimes within a short time but in extreme instances several days after the disaster.

The men who survive a disaster may be regarded as prisoners within a mine. They may have been forced to barricade themselves in to prevent the afterdamp from reaching them, or they may be penned behind falls of rock or coal which have blocked the only roadway leading to the mine mouth. Again, certain sections of the mine may be isolated from others by fire or flood. Often the usual means of communication is destroyed or made ineffective. Under such circumstances rescuers, relatives, and friends have no means of communicating with the imprisoned men. No word as to the number of men alive can reach those waiting outside, no word of encouragement can be given those entombed, and no directions can guide the searching crews in their rescue efforts. The last factor is the most regrettable of all, as in a number of disasters prompt arrival of rescue crews at places where men were entombed would have prevented death.

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The chief purpose of Bureau of Mines experiments in underground communication has been to seek out and, if possible, devise some practical means of communicating with entombed miners, not only to give them comfort and assurance but also to direct early rescue work which may save lives.

The problem of communication after a disaster has always been regarded by the Bureau as extremely difficult to solve. Miners work under a great variety of conditions. Mines vary in depth from the shallow surface coal beds in Pennsylvania to the deep copper deposits in Michigan. Mines are of various sizes, from mere holes (small wagon mines) to the vast excavated areas of some of the large coal or metal mines. Large mines have numerous passageways, some of them miles long, a labyrinth of interconnected underground workings which seem like a maze to persons unfamiliar with mining methods. The strata through which signals must be sent not only vary in depth but are made up of many kinds of earthy matter, often interspersed with water-bearing beds. Another difficulty is that apparatus used in mine rescue work must of necessity be extremely simple and of light weight.

The various phases of the general problem of underground communication have embraced investigations by the Bureau of Mines covering about six years.

Many of the American bituminous coal mines are much shallower than the coal mines of Europe or some of those in the anthracite region of Pennsylvania; it was therefore believed that a signal which would penetrate at least 400 feet of strata overlying a mine would serve a large proportion of the American coal mines. Hence, this figure was used as a measure of the practicability of any given signaling scheme. Any reliable means of communication was believed worth consideration, but two-way voice communication was believed most desirable; moreover, one-way voice communication, especially from the outside to the inside of the mine, was thought preferable to a straight code system

As the result of the Bureau's investigations, two methods

of underground communication seem to promise usefulness: First, the geophone or earth-vibration method, and, second, the grounded-line or roof-rail conduction method of communication with telephones.

In the earth-vibration method the transmitter is a sledge or rock and the receiver is a geophone. The simplicity and availability of the transmitter are readily conceded. The receiver (geophone) is simple, but efficient operation requires a certain degree of skill. The greatest drawback to the geophone method is that voice communication is impossible, and the use of code to any extent is difficult. The transmitter in the roof-rail system of communication is an ordinary microphone transmitter used straight or with amplification. This apparatus is fairly simple—in fact, simpler than the geophone—except possibly when amplification is used. The receiver is about the simplest of all, being only a watchcase-type telephone receiver. The wiring system inside the mine is very short, extending from the roof to the rail or floor connections. The roof connection for receiving is very simple, but for transmitting the connection has to be more extensive because the current flowing is many times that in reception. At the surface the roof-rail system requires an insulated line from the nearest available connection to the mine floor or track to a point within a radius of approximately 500 feet over the place in the mine where the underground station is located. As this line is on the surface, however, it should involve no difficulty. The roof-rail method employs either voice or code.

In these facts concerning the two possible systems of communication two things are noted: First, the system using the geophone has much the simpler transmitting apparatus, whereas the system using telephones employs the simpler receiving apparatus with relation to conditions underground. It naturally follows, therefore, that a combination of the two systems might be more practical than either one alone. In such a composite system the underground transmitter would be a sledge, rock, etc., and the receiver would be a simple watchcase-type telephone receiver. The transmitter at the

surface would be a telephone and the receiver a geophone, possibly with amplification for both for the greater distances. The transmitter in the mine would therefore always be within reach of the entombed men, and the watchcase receiver could be incorporated in the miner's first-aid pack. This combination would allow voice one way—that is, into the mine—and rudimentary code from the mine to the surface. However, this should be ample for rescue purposes and much more satisfactory than code both ways.

The use of a combination method, however, would depend upon further development of these two systems of underground communication. The geophone has been developed so as to penetrate a depth of 550 feet without amplification. The few tests made with the telephonic method have shown the possibility of penetrating depths of more than 430 feet at a distance of more than 1,700 feet from the shaft with no amplification. Only enough work has been done on this latter system, however, to indicate its possibilities.

The theory and practice of geophysical prospecting for minerals and oil elucidate more fully all the methods of underground communication studied by the Bureau, with the exception of line radio. It is a fact, however, that the power used in geophysical prospecting is much greater than that possible in underground communication through earth strata for rescue purposes. Thus geophysical prospecting, in a way, amplifies the Bureau's deductions.

It is possible that further studies in electrical prospecting will bring out some practical use of radio for underground communication work, although the Bureau feels that, owing to the limitations specified for mine-rescue apparatus, this is rather improbable.

LIMITS OF INFLAMMABILITY OF GASES AND VAPORS.

A STUDY of the limits of inflammability of a large number of gases and vapors has been made by the United States Bureau of Mines, Department of Commerce. A knowledge of the limits of inflammability of methane, and indeed of the

products of distillation of coal, in air and in partly vitiated atmosphere, is of fundamental importance in the study of mine explosions and their prevention. Likewise, a knowledge of the inflammable limits of gasoline and benzol vapors, natural and manufactured gas, blast-furnace gas, hydrogen, acetylene, and many other gases is of equal importance in the prevention of gas explosions and fires in the metallurgical, petroleum, gas-manufacturing, and related industries.

Substances that a short time ago were found infrequent, even in the laboratory, are being used on a large scale, and some of them form dangerously explosive mixtures with air. Data concerning their limits of inflammability are widely scattered in the literature, and many of the figures seem contradictory. The results of the Bureau's comprehensive survey have been published in Bulletin 279, by H. F. Coward and G. W. Jones.

An inflammable mixture of gases, such as methane and air, may be diluted with one or the other of its constituents or with other gases until a composition is reached which is no longer inflammable. The dilution limit of inflammability, or simply the limit of inflammability, is the border-line composition; a slight change in one direction or the other produces a mixture which is accordingly inflammable or non-inflammable.

There are clearly two limits of inflammability, a higher and a lower, for each pair of so-called combustible gas and supporter of combustion. The lower limit corresponds with the minimum amount of combustible gas, the higher, or upper, limit with the maximum amount of gas capable of conferring inflammability on the mixture. For example, for methane-air mixtures these limits under normal conditions are approximately 5 and 14 per cent. methane, respectively; compositions between these figures liberate enough energy on combustion of any one layer to ignite the neighboring layer of unburned gas and are therefore capable of self-propagation of flame; others are not. Mixtures richer than 14 per cent. methane, however, may burn on contact with external air, for other mixtures which are inflammable, containing between 5 and 14 per cent. methane, are thus formed.

The experimental determination of limits of inflammability is more difficult than may be anticipated, as is shown by the contradictory figures reported from time to time. It is the object of this bulletin to present the results of a critical review of all figures published on the limits of inflammability of combustible gases and vapors when in admixture with air, oxygen, or other "atmosphere." Suspended dusts and liquid mists are not considered

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A RAPID CORROSION TEST FOR GASOLINE.

FOR the proper control of gasoline treating plants there is need of a quick test for corrosion. In "sweetening" gasoline, that is, in treating it to remove evil-smelling mercaptans or to convert them to disulphides or sulphides, the sodium plumbite ("doctor") method is generally used. This method involves agitation of the gasoline with "doctor solution" (sodium plumbite made by dissolving litharge in a solution of caustic soda) in the presence of free sulphur. One of the common mistakes in the technique of this process is the addition of too much free sulphur, which will dissolve in the gasoline and cause it to be corrosive. In the operation of a continuous sweetening or treating plant, a check on the corrosiveness of the product is imperative at all times. The copper-strip test commonly used in specifications takes so long to perform that the plant may fail to function properly for some time before the operator discovers it.

The Bureau of Mines has investigated a recently developed rapid corrosion test method involving the use of metallic mercury, which has been used successfully for several months in controlling the operation of continuous treaters and which seems to have several advantages over the copper-strip test. Chief among these is the time saved, as the copper-strip test takes at least one-half hour, while the mercury test can be made in about five minutes. It is very evident that this is an important item in controlling a continuous treater.

A 100-c.c. sample of the gasoline drawn from the treater is placed in a clean 4-ounce sample bottle and 1 c.c. of metallic mercury added. The bottle is shaken uniformly for two minutes, and the gasoline decanted off and filtered at once through an 8-inch qualitative filter paper. he filter paperT is then dried by an electric fan or by natural evaporation.

The intensity of the black precipitate on the paper is a measure of the corrosiveness of the gasoline. A clean paper or one that is only slightly discolored indicates that the gasoline will pass the copper-strip test. If there is a heavy black precipitate on the paper and the sample is negative to the doctor test, it indicates that an excess of sulphur over that needed to complete the reaction has been added and that the gasoline will be corrosive.

The operator or chemist may have to compare the mercury and copper-strip tests of a few samples to interpret the former in terms of the latter, but after a little experience he should have no difficulty with this.

Five minutes usually is enough for completing the test. Thus the operator of the treating plant can know within five minutes from the time he starts his test whether or not he has added too much sulphur.

The mercury in this test can be used over and over again. When the mercury becomes dirty from particles of sulphides it may be cleaned by shaking with a few cubic centimeters of strong hydrochloric acid, washed with water, and dried on a filter paper, or it may be filtered through chamois. Tests can be made at regular intervals, and the filter sheets from the tests can be marked according to time and other data and posted on a board in the laboratory or at the treating plant; thus the chemist or operator can see at a glance how the treater is functioning and make changes to correspond.

The test seems to be more severe than the copper-strip test, as a perfectly clean paper is seldom obtained; but the range or gradations are much greater, which should allow much better control of the treating plant.

This test may also be used in testing the corrosion of gasolines that are too volatile to run by the copper-strip method.

This test seems to offer possibilities, especially in the control of continuous sweetening plants using the sodium plumbite method of sweetening and in testing the corrosion of very volatile gasolines.

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Meeting held Wednesday, April 18, 1928.)

THE regular monthly meeting of the Institute was called to order at three-thirty p.m. by the Senior Vice-President, Mr. Henry Howson.

The Secretary announced that the minutes of the March meeting of the Institute had been printed in full in the April number of the JOURNAL and moved that these minutes be approved as printed. The motion was seconded and unanimously adopted.

The Secretary made a report concerning changes in membership since the preceding report. The following elections have been made: nine Resident, six Non-Resident, three Student. During the same interval the deaths of six members of the Institute occurred.

The following report of a Special Committee, consisting of W. H. Fulweiler, Chairman, Dr. Henry Leffmann, and Dr. George F. Stradling, appointed at the stated meeting of The Franklin Institute held Wednesday, February fifteenth, has been presented. It is a minute expressive of the sentiments of the general membership of the Institute concerning the death of the President of the Institute, Dr. W. C. L. Eglin. It is to be spread upon the minutes of the meeting and a copy of it is to be sent to the family of Dr. Eglin.

Your Committee appointed at stated meeting held February 15, 1928, to prepare minute upon the death of Dr. Wm. C. L. Eglin, begs to submit the following proposed minute:

> In the death of Dr. Wm. C. L. Eglin The Franklin Institute loses one who has devoted his best thought and endeavor to the growth and prosperity of The Franklin Institute since his association with it in 1891.
>
> Since Dr. Eglin's election as President of the Institute in 1924, much of the progress of the Institute has been due to his capable leadership and the wisdom he has brought to bear upon the numerous problems of the Institute.
>
> Notable in the work of Dr. Eglin was his successful direction of the Centennial of the Institute in 1924. His efforts in bringing together a distinguished group of scientists who took part in the commemorative exercises, his qualities as a host and his executive ability contributed to make the celebration noteworthy.
>
> To be mentioned particularly among the good works that Dr. Eglin has accomplished for the benefit of The Franklin Institute are the Christmas Week Lectures for young people, from which much fruit has been derived.
>
> The membership at large of the Institute desire to indicate their appreciation of Dr. Eglin's long and useful services to the Institute and to express their sorrow at his death and to extend their most sincere sympathy to his family.

The Secretary stated that the Board of Managers recommended the election to Honorary Membership in the Institute of Dr. Charles Francis Brush of Cleveland, Ohio, and Professor Doctor Walther Nernst of Berlin University, Germany,

to whom Franklin Medals have been awarded and are to be presented at the Medal Day meeting on May sixteenth. The meeting unanimously, by rising vote, adopted this recommendation of the Board of Managers, and the two gentlemen were declared elected to Honorary Membership.

The Secretary then read notices concerning an open meeting of the Committee on Science and the Arts to be held on Wednesday, May second; concerning the Medal Day exercises; and concerning the showings of the museum film for the benefit of the general membership of the Institute.

There was no further Institute business and the programme of the day followed.

The Senior Vice-President, Mr. Howson, presented Dr. Charles F. Brush of Cleveland, Ohio, who talked on "Some Reminiscences of Early Electric Lighting." The paper by Dr. Brush was followed by a paper by Dr. Elihu Thomson of Lynn, Massachusetts, on "The Pioneer Investigations on Dynamo Machines Fifty Years Ago."

The Secretary of the Institute showed photographs illustrating the developments in dynamo construction of the last fifty years and expressed the appreciation of the Institute for the talks delivered by the two speakers of the day.

As there was no further business the meeting adjourned at four-fifty-three p.m.

HOWARD MCCLENAHAN,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, April 4, 1928.)

HALL OF THE COMMITTEE,
PHILADELPHIA, April 4, 1928.

DOCTOR GEORGE S. CRAMPTON *in the Chair.*

The following reports were presented for first reading:

No. 2877: Improved Refractometer.

This report recommended the award of the Edward Longstreth Medal to Mr. Warren P. Valentine of Philadelphia, Pa., "In consideration of the meritorious work shown in the improvement of the mechanical and optical parts of the Abbe Refractometer, thereby increasing its accuracy."

After a discussion in which the fact that Mr. Valentine makes the prisms for this instrument was brought out, the report was passed to a final reading and on motion was adopted.

No. 2892: Work of Mr. William F. Kiesel, Jr.

This report was presented for first reading and on motion was passed to a final reading, the report recommending the award of the George R. Henderson Medal to Mr. William F. Kiesel, Jr., of Altoona, Pa., "In consideration of his numerous inventions of outstanding value in locomotive and railway car design and construction."

GEO. A. HOADLEY,
Secretary to Committee.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, April 11, 1928.)

RESIDENT.

MR. HENRY CREWDSON, Mechanical Engineer, Viscose Company, Marcus Hook, Pa.

DR. WALTER ARCHER MACNAIR, Physicist, Victor Talking Machine Company, Camden, New Jersey.

DR. FRED PAUL NABENHAUER, Research Chemist, 35 Poplar Street, Philadelphia, Pa.

MR. EDMUND RICHARD THEWS, Consulting Metallurgist, 950 Mulford Building, Fifteenth and Wallace Streets, Philadelphia, Pa.

NON-RESIDENT.

MR. BENJAMIN HEAP, Analytical Chemist and Works Superintendent, The Chloride Electrical Storage Co., Ltd., Clifton Junction, near Manchester, England.

MR. H. W. MAJOR, Manufacturer of Fishing Tackle, 250 East Seventh Street, Long Beach, California.

CONTRIBUTING.

Representing Leeds and Northrup.

MR. M. J. BRADLEY, 4901 Stenton Avenue, Philadelphia, Pa.

CHANGES OF ADDRESS.

MR. ROBERT R. ABBOTT, 2938 Berkshire Road, Cleveland, Ohio.

H. CARL ALBRECHT, ESQ., Assistant Operating Manager, Philadelphia Electric Company, 1000 Chestnut Street, Philadelphia, Pa.

MR. CHARLES E. BONINE, 1404 Franklin Bank Building, 1417 Sansom Street, Philadelphia, Pa.

DR. ALLERTON S. CUSHMAN, 250 Park Avenue, New York City, N. Y.

MR. CHARLES ENGELHARD, Charles Engelhard, Inc., 90 Chestnut Street, Newark, New Jersey.

MR. ARTHUR FALKENAU, 40 Earle Place, New Rochelle, N. Y.

MR. I. H. FRANCIS, 1520 Locust Street, Philadelphia, Pa.

MR. HENRY KIPPENBERG, Starnberg bei München, Vordere Mühlbergstrasse 1, Germany.

DR. RALPH H. MULLER, Department of Chemistry, Washington Square College, New York University, Washington Square, East, New York City.

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NECROLOGY.

Gaetano Lanza, engineer, born in Boston, September 26, 1848, died in Philadelphia, March 21, 1928. He was educated in Virginia and received his professional training at the University of Virginia. The degree of Civil Engineer was conferred upon him by that institution in 1869 and in the following year he received also the degrees of Bachelor of Science and Mechanical Engineer.

For two years he served as assistant instructor in mathematics at the University of Virginia and in 1872 he received his first appointment at the Massachusetts Institute of Technology. For nearly forty years he was connected with this institution, first as instructor and assistant professor, then as professor of theoretical and applied mechanics, and from 1883 to 1911 he was in charge of the Department of Mechanical Engineering. In the latter year he was made emeritus professor.

He came to Philadelphia and became special consultant for the Baldwin Locomotive Works.

He was the author of several works on mechanics, his best-known being "Applied Mechanics," first published in 1885.

Professor Lanza was a member of the leading engineering societies of the world. He became a member of The Franklin Institute in 1912 and for a number of years was one of the Associate Editors of the JOURNAL OF THE FRANKLIN INSTITUTE.

Theodore William Richards, Ph.D., LL.D., Sc.D., Ch.D., M.D., was born in Philadelphia, January 31, 1868, and died at Cambridge, Mass., on April 2, 1928. He was educated by private tutors and at the age of fifteen became a sophomore at Haverford College, where he devoted most of his time to the study of chemistry. Two years later he entered the senior class at Harvard University, graduating in the following year with highest honors in chemistry. In 1888 he received the degree of Master of Arts and Doctor of Philosophy from the same institution. After spending a year in study in Europe he returned to Harvard University as assistant in chemistry, later becoming professor of chemistry and after the foundation of the Wolcott Gibbs Memorial Laboratory he was appointed its director.

His activities were not confined to any one branch of chemical investigations but he is best known for his researches on the atomic weights of more than twenty elements.

He was the recipient of the Davy Medal of the Royal Society, 1910, Faraday Medal of the Chemical Society, 1911, Willard Gibbs Medal of the American Chemical Society, 1912, The Franklin Medal, 1916, Le Blanc and Lavoisier Medals, 1922, and the Nobel Prize in Chemistry in 1914.

Mr. Henry M. Canby, Wilmington, Delaware.
Mr. Albert W. Smith, Cleveland, Ohio.
Hon. W. C. Sproul, Philadelphia, Pa.

LIBRARY NOTES.

RECENT ADDITIONS.

BUCKINGHAM, EARLE.—Spur Gears. 1928.

Colloid Symposium Monograph, Volume 5, Edited by H. B. Weiser. 1928.

COLVIN, FRED H. AND HENRY F.—Aircraft Handbook. Third edition. 1928.

FERNALD, R. H., AND G. A. ORROK:—Engineering of Power Plants. Third edition. 1927.

FORD, HENRY, in collaboration with SAMUEL CROWTHER.—My Life and Work. 1926.

Fundamentals of Dairy Science, by the Associates of Lore A. Rogers. 1928.

International Critical Tables of Numerical Data, Physics, Chemistry and Technology. Volume 3. 1928.

London, Metropolitan Water Board. Twenty-fourth Annual Report, 1926–27.

PAGÉ, VICTOR W.—Modern Aircraft. 1928.

RAWDON, HENRY S.—Protective Metallic Coatings. 1928.

SPOONER, THOMAS.—Properties and Testing of Magnetic Materials. First edition. 1927.

THOMSON, G. P.—Applied Aerodynamics. No date.

WALL, T. F.—Applied Magnetism. 1927.

WILSON, SAMUEL P.—Pyroxylin Enamels and Lacquers. Second edition, enlarged. 1927.

BOOK REVIEWS.

THE CHEMISTRY OF LEATHER MANUFACTURE. By John Arthur Wilson, Chief Chemist, A. F. Gallun & Sons Co. (Tanners), Milwaukee, Wisconsin. Second Edition, Volume I, American Chemical Society, Monograph Series No. 12. 495 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1928. Price, $10.

"Nothing like leather" is an old saying. The story of its origin need not be here repeated as it is probably not true. The preparation of animal skins for human use must date back to a very remote past. Even nations that are now in very primitive conditions are familiar with methods by which skins can be permanently preserved and more or less decorated. Up to a comparatively recent period the manufacture of leather was largely dependent upon empiric systems. It was a trade carried on from master to apprentice and based upon traditional standards. There is a reference in the New Testament to the house of Simon the Tanner and there are many other references in ancient literature. The principal method of preparing leather in civilized countries in more modern days has been the use of materials containing tannin. As with other great industries, chemical investigation began many years ago and has finally been brought to a very high degree of excellence. The crude and rough methods of tanning with natural products have given way to the employment of specific chemicals and have thus put upon the market a considerable variety of leathers adapted to special purposes.

The present volume covers the chemistry and physical chemistry of leather

manufacture by means of the vegetable tanning materials. It is very comprehensive in its scope, discussing first the histology of the skins, their chemical constitution, the physical chemistry of the protein materials, and in detail all the procedures from the raw skin to the finished product. There is also included a chapter on the nature and composition of the vegetable tanning materials and their valuation both as original substances and in their applications to the manufacture of leather. There is a very large amount of modern chemistry and physical chemistry included in the text and the work is illustrated with a number of very fine engravings of tissues under magnifying power. It will therefore constitute a manual of instruction to all who are engaged in the manufacture of leather.

HENRY LEFFMANN.

COLLOID SYMPOSIUM MONOGRAPH. Edited by Henry Boyer Weiser, Professor of Chemistry, The Rice Institute, Houston, Texas. 394 pages, 8vo. New York, The Chemical Catalog Company, Inc., 1928. Price, $6.50.

Primarily, a symposium is a drinking bout, but although the participants in the fifth national colloid symposium, of which this volume is a report, were made comfortable at Ann Arbor where the meeting was held, the "feast of reason" was the exclusive feature. The complicated problems of colloid chemistry were presented in a great variety of forms, but in some respects the present volume is different from much of the material offered in works upon the subject. Considerable space is given to the relations of physiologic processes to colloid chemistry and physical chemistry. Noticeable in this respect is an article on the relation of hydrophilic colloids to the hardiness of winter insects. Several species of insects were tested with carefully constructed apparatus and it was found that "bound water" and water adsorption have important influences on the power of both plants and animals to withstand cold.

Another paper of special type is on adsorption and crystal form. It is somewhat refreshing to note references to crystals in a work on colloids. Reference is made in the beginning of the article to the long known fact that while a pure sodium chloride solution will give cubes the addition of urea will produce marked octahedral faces. Other additions such as free alkali will also bring about modifications. The article discusses the physical chemistry of these influences. The result of careful and elaborate research is to show that a new technic has been developed by which the influence of impurities on crystal forms can be predicted. This is a matter which will interest mineralogists, who are now paying greater attention than ever to the question of mineral forms.

Many other interesting and important contributions are to be found in the volume, which exhibits the excellent composition and press-work of the well-known publishing company.

HENRY LEFFMANN.

COURS D'ÉLECTRICITÉ THÉORIQUE, PROFESSÉ A L'ÉCOLE PROFESSIONNELLE SUPÉRIEURE DES POSTES ET TÉLÉGRAPHES. Par J. B. Pomey, Ingénieur en Chef des Postes et Télégraphes. Vol. II, 373 pages, 25 x 16 cm., paper. Paris, Gauthier-Villars et Cie, 1928. Price, 100 francs.

More and more are engineers, particularly those who deal with electrical subjects, called upon to apply types of mathematical processes in the solution of

the problems of their art in which formerly only mathematical specialists were proficient. Gradually, as the results of recent mathematical investigation and experimental verification have assumed definite form, many of these processes have come into use in engineering texts. To a greater degree than most others of its type, this work which develops electrical theory without losing contact with the practical aspects of the subject is especially liberal in the use of such mathematical devices. Accordingly a very substantial mathematical preparation on the part of the reader is presupposed.

The author begins with an examination of the variable period of current-increment in a cable by the method which he communicated to the Institut bearing the date of May 1st, 1911 in which he shows the relations which exist between the divers forms of solution and the theta-functions of Jacobi. It being necessary to harmonize the telegraph equation with the results of an examination of the electromagnetic field in the vicinity of a cylindrical conductor, the conditions of this verification are prescribed after the methods of Poincaré. Proceeding to stable periodic conditions, he introduces the electromotive waves conceived by M. Aguillon, chief-engineer of the bureau of telegraphs. He gives a diagram which illustrates this theory, and defines the phenomena of reflection which are produced at the junction of two lines which have different properties.

Two-wire artificial lines have recently been given the name "quadripole." He has drawn for this chapter on articles which have appeared in *Telegraphen und Fernsprechtechnik*, on the writings of Breisig and of K. S. Johnson and on the memoirs of Plejel. Among these quadripoles may be recognized electric filters which are proving so useful in wireless and in cable transmission. An outline of pupinization is given, then the theories of the telephone of Poincaré and Kennelly. These lead to an equation of an electro-mechanical quadripole.

The conditions requisite for the generation of oscillations in a circuit in which the resistance may become negative is treated according to the method of MM. Élie and Henri Cartan who have rigorously demonstrated how oscillations are generated and how they tend to assume a stable periodic condition. The author then considers in a summary manner the propagation of electric waves in space; he defines the velocity of a signal as that of the propagation of a disturbance which affects the carrier-wave. He makes a comparison between electric energy and elastic energy in order to emphasize the differences peculiar to each. Then he considers the conception of internal energy of a system of magnets and currents after the notable work of M. Liénard. The volume concludes with a summary of molecular theories of magnetism.

As may be gathered from the above citations, there is much in the book which has as yet only appeared in the form of memoirs while original methods are employed in the discussion of other topics. Telegraph engineers and others interested in the propagation of electric currents will accordingly find this work a fertile source of recent record of progress in this important branch of their art.

L. E. P.

ÉLÉMENTS DE THERMODYNAMIQUE. Par Charles Fabry, Membre de l'Institut, Professeur à la Sorbonne et à l'École polytechnique. 216 pages, 17 x 11 cm., paper. Paris, Armand Colin, 1928. Price, 9 francs.

The importance of the energy relationships of thermal phenomena in every branch of physics has long been well-appreciated and thermodynamics over a

long period of years has received a very full share of refinement of presentation in the hands of many eminent writers. Professor Fabry under whom students at the two famous schools, the Sorbonne and the École Polytechnique, have had the good fortune to study that subject, has had the happy inspiration to contribute an abridgment of this course of study to the collection of scientific texts of the Armand Colin series.

In that form, we have a text that is not only of rare value for a first acquaintance of this abstract subject, but one whose treatment is in adequate detail to furnish a working knowledge of principles which are applicable to many of the requirements of practice. Moreover there are doubtless many readers of the more exhaustive treatises whose task will be much lightened by a reference to this unusually lucid presentation. The work is a notable addition to the valuable series of condensed texts to which it belongs.

LUCIEN E. PICOLET.

APPAREILS ET MÉTHODES DE MESURES MÉCANIQUES. Par le Lt.-Colonel Jules Raibaud, Chef des Travaux pratiques de Mécanique à l'Ecole Polytechnique. (No. 99, Collection Armand Colin.) 215 pages, 17 x 11 cm., paper, illustrated. Paris, Librairie Armand Colin, 1928. Price, bound, 10 f. 25, paper 9 f.

Most of the data available on the apparatus and methods applicable to the measurement of the innumerable variety of quantities which occurs in scientific investigation or in the industries are to be found in treatises on each particular type of such activity. Notable among these are the several works on experimental engineering and works on machine-shop practice, to say nothing of the well-illustrated catalogues of manufacturers of measuring appliances used in the machine-shop.

The present volume is designed to present in compact form the principles and methods of effecting the purely mechanical measurements in the engineering laboratory. The topics are: Time, velocity, acceleration, mass, force, pressure, work, elastic magnitudes, and an appendix on correlative units of measure. It will be noted that no appliances for measures of length or methods of precise gauging are included. There are no complete apparatus described, only principles are discussed which are adequately illustrated in diagrammatic form. The author's attention is called to an error in the diagram Fig. 51a. The bob-weight and scale-arm should be interchanged to obtain the tangent relation stated; as shown it is quite inoperative.

It is obviously impossible in a book of this kind to treat in more than a summary manner each of the topics noted which would require a volume of considerable size for full treatment, but it has much suggestive value to the technologist and is an excellent outline for a general view of the subject.

LUCIEN E. PICOLET.

PUBLICATIONS RECEIVED.

Colloid Symposium Monograph. Papers presented at the Fifth National Symposium on Colloid Chemistry, University of Michigan, June 1927. Edited by Harry Boyer Weiser. 394 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1928, price $6.50.

Elements of Machine Design, by James D. Hoffman, M.E., and Lynn A. Scipio, M.E. 327 pages, illustrations, 8vo. Boston, Ginn and Company, 1928, price $3.80.

The Chemistry of Leather Manufacture, by John Arthur Wilson. American Chemical Society Monograph, No. 12. Second edition, volume one. 495 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1928, price $10.00.

National Electrical Safety Code. Fourth edition, December 31, 1926. Handbook series of the Bureau of Standards, No. 3. 525 pages, diagrams, tables, 12mo. Washington, Government Printing Office, 1927, price $1.00.

How to Build and Operate "The Wireless World" Moving Coil Loud Speaker. Complete constructional details and dimensional drawings by F. H. Haynes, assistant editor. 32 pages, illustrations, 8vo. London, Iliffe and Sons, Ltd., 1928, price 1 shilling, 6 pence.

Crystallographic Tables for the Determination of Minerals, by Victor Goldschmidt (Heidelberg) and Samuel G. Gordon (Philadelphia). Special Publication No. 2, The Academy of Natural Sciences of Philadelphia. 70 pages, 8vo. Philadelphia, 1928, price $1.50.

The Chemical Effects of Alpha Particles and Electrons, by Samuel C. Lind, Ph.D. American Chemical Society Monograph Series No. 2. Second (revised and enlarged) edition. 252 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1928, price $5.00.

The Elements of Economic Geology, by J. W. Gregory, D.Sc. 312 pages, illustrations, 12mo. New York, E. P. Dutton and Company, 1928, price $3.25.

La Théorie de la Relativité et la Mecanique Céleste, par Jean Chazy. Tome I. 261 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1928, price 60 francs.

Mémorial des Sciences Physiques, publié sous le patronage de l'Academie des Sciences de Paris. Fascicule I, La mécanique ondulatoire par M. Louis de Broglie, 55 pages, 8vo. Fascicule II, La télémétrie monostatique par M. Armand de Gramont. 64 pages, illustrations, plate, 8vo. Paris, Gauthier-Villars et Cie., 1928, price, per part, fifteen francs.

Kathodenoszillograph, von Prof. A. Matthias und Dr. Ing. D. Gábor. Sonderheft, Forschungshefte der Studiengesellschaft für Höchstspannungsanlagen. 77 pages, illustrations, quarto. Berlin, Vereinigung der Elektrizitätswerke e. V., 1927, price 12 marks.

Report of a Survey of Transportation on the State Highways of Vermont, by the Bureau of Public Roads, U. S. Department of Agriculture and the Vermont State Highway Department. 80 pages, illustrations, maps, quarto.

Report of a Survey of Transportation on the State Highways of New Hampshire, by the Bureau of Public Roads, U. S. Department of Agriculture and the New Hampshire State Highway Department. 79 pages, illustrations, map, quarto, 1927.

National Advisory Committee for Aëronautics, Technical Notes. No. 279, Resistance of Streamline Wires by George L. De Foe, 7 pages, diagrams, quarto. No. 280, Drag of Exposed Fittings and Surface Irregularities on Airplane Fuselages by Donald H. Wood, 10 pages, illustrations, quarto. No. 281, A Comparison of Propeller and Centrifugal Fans for Circulating the Air in a Wind Tunnel by Fred. E. Weick, 7 pages, illustrations, quarto. Washington, Committee, 1928.

CURRENT TOPICS

New Results on Cosmic Rays. R. A. MILLIKAN and G. H. CAMERON. (*Nature*, Jan. 7, 1928.) This is the report of an evening lecture given by Prof. Millikan at the meeting of the British Association for the Advancement of Science last summer. He limits the application of the term 'cosmic rays' to the small part of 'penetrating radiation' that is of cosmic origin. Not all physicists were convinced a year or two ago of the existence of cosmic rays. Besides this there has been a very wide divergence between the estimates of the intensity of this problematical radiation furnished by Hoffmann, Swann, Kohlhoerster and the California investigators.

In 1903 McLennan, Rutherford and others found that the rate of discharge of electroscopes near the earth could be considerably retarded by surrounding them with one layer of lead after another. This observation demonstrated the existence of 'penetrating radiation.' In 1910 Gockel, having used an enclosed electroscope in a balloon 4,500 meters above the earth's surface, discovered that at this altitude the penetrating radiation was more intense there than at the surface. This suggested that at least some of this radiation came into the atmosphere from above, an origin proposed four years earlier by Richardson. Two others, Hess and Kohlhoerster separately confirmed his results. The latter announced that the intensity of the radiation decreased from the earth up to 1,000 m. and then increased up to 9,000 m. where it was about seven times as great as at the surface. The war caused a hiatus in experimenting but in 1921 and 1922 Millikan and Bowen sent up sounding balloons to an elevation of nearly 10 miles. Their instruments left below them nine-tenths of the mass of atmosphere and by their readings testified to the general correctness of the increasing discharge rate predicated for high altitudes. It was, however, found that the rate at the highest points reached was not as large as would have been predicted from Kohlhoerster's figures, "thus showing that the 'penetrating rays,' *if they come from above*, were actually more penetrating than had been supposed up to that time." The summer of 1923 was fruitful in the measurement of coefficients of absorption of the penetrating rays in substances other than the air. Kohlhoerster from experiments on the shielding power of Alpine

glaciers deduced an absorption coefficient of .25 per meter of water. This quantity removed the discrepancy between the results of his balloon observations and those made in America. Millikan and Otis worked on the top of Pikes Peak, surrounding their instruments with thick lead screens. They concluded that "if any of the penetrating rays which they found on the Peak were of cosmic origin they had to be more penetrating, or less strong, than corresponded even with the reduced values found by Kohlhoerster." They discovered no new evidence of the existence of cosmic rays. "Indeed, up to 1925, there appears from the literature to have been no feeling of certainty in any quarter that the existence of cosmic rays had been proved." Hoffmann in Germany and Swann in America had obtained experimental results seemingly incompatible with the presence of such rays.

In 1925 Millikan and Cameron sunk sealed electroscopes in deep lakes fed by snow water. Ordinary lakes are contaminated by radioactive substances derived from the earth's crust. The ionization at the surface of Muir Lake, altitude 3,590 m., amounted to 13.3 ions per c.c. per sec. As the electroscope descended into the water the number of ions diminished regularly to 3.6 ions at a depth of 18 m. Below this level no further decrease could be noted. "This was the first time the zero of an electroscope—the reading with all external radiations completely cut out—had been definitely determined." The observations proved one of two things, the presence at the surface of the lake of a radiation that could pass through 18 m. of water before all of it was absorbed or some remarkable distribution of radioactive material in the water. To discriminate between these two possibilities similar experiments were repeated in a second snow-fed lake 300 miles south of Muir Lake and 2,060 m. lower in altitude. The two sets of observations agreed thoroughly. The 2,060 additional meters of air through which radiation had to pass in going from the level of Muir Lake to the surface of the second body of water was in theory equivalent in absorbing power to 1.8 m. or 6 ft. of water and it was found that the ionization at a level in the second lake was in general equal to that occurring at a level in Muir Lake 6 ft. nearer to the surface of its water than was the level of comparison in the lower lake to its surface. Thus was ruled out the hypothesis of strange radioactive distribution in Muir Lake. In addition it could not be maintained that the rays in question had their origin in the atmosphere lying between the levels of the

two lakes, because this intervening layer of air comported itself as a passive, absorbing blanket, acting in all ways as if the rays came from above. Besides it was shown that the rays were just alike at the same altitude for places 300 miles apart. These facts joined to the absence of evidence that the intensity of the rays varies with the part of the sky above the post of observation indicates that the rays that are present at high altitudes do not originate in the atmosphere or at least in the lower part of it.

In 1926 experiments were carried out in the Bolivian Andes at an elevation of 3,800 m. or more. Determinations at Lake Titicaca and at a higher body of water agreed with what had been found in the Northern Hemisphere. This coincidence of result rendered improbable the production of 'cosmic radiation' by the impact of high-speed beta rays upon the outer layers of the atmosphere, since such a method of production would be expected to be more intense near the earth's magnetic pole than near its equator. C. T. R. Wilson had advanced a suggestion that the rays were due "to the integration of the effects of the impact in the earth's atmosphere of electrons endowed with many millions of volts of energy acquired in thunderstorms." There was good agreement between the ionization results gotten on Lake Miguilla, shut in by high mountains and therefore shielded from the effects of thunderstorms, and those obtained in California. The authors believe that Wilson's hypothesis may be rejected.

As a part of the work of the expedition to South America a careful study was made of change of intensity in connection with the part of the sky above the station "We took two long series of observations, each lasting three days, at an altitude of 15,400 ft. (4,620 m.) in a deep valley from which the Milky Way was in sight for a period of 5 or 6 hours and then practically out of sight for another 6 hours. We could detect no difference at all in the value of the readings when the Milky Way was overhead and when it was out of sight." In this they agree with Hoffmann and Steinke but are opposed to Buettner and Kohlhoerster. The authors emphasize the need of settling this point definitely as an important preliminary step to locating the source of the rays.

In 1926 the authors had much more sensitive electroscopes constructed and with them resumed the study of 'cosmic radiation' in California. Instead of the submerged instrument reaching a steady state of ionization when it was 60 ft. below the water surface it continued to indicate reduction of

ionization until a depth of 164 ft. was attained. "Taking into account the absorption of the atmosphere above Gem Lake, which is the equivalent of 7.45 meters of water, the new experiments reveal rays so penetrating as to pass through 57 meters (190 ft.) of water, or 5 m. (16.7 ft.) of lead before being completely absorbed." A study of the absorption indicates the presence in the radiation of wave-lengths from .00053 to .00021 A.

The cosmic rays may be produced by the impact of rapidly moving electrons upon atomic nuclei. "These rays must come in the main from beyond the Milky Way." The influx of energy at the outer layer of the earth's atmosphere amounts to 3.1×10^{-4} ergs per sq. cm. per sec. or 1/10 of the influx of light and heat from the stars.

G. F. S.

Oregon Great Power State.—The potential water-power resources of Oregon amount to 3,665,000 horsepower as estimated from the stream flow available 90 per cent. of the time, or 5,890,000 horsepower as estimated from the flow for 50 per cent. of the time, if storage is provided in feasible reservoir sites, according to a statement made public by the Department of the Interior based on field work and studies of the Geological Survey. River surveys have been made and maps published by the Geological Survey covering 1,674 miles of rivers in Oregon. The river surveys included a number of reservoir sites, and in addition 47 dam sites were surveyed on a large scale.

Some idea of what nearly 6 million horsepower of potential water power in the rivers of Oregon may mean to the future of the State can be gained from the fact that so far only about 3 per cent. of these water-power resources have been utilized and that with complete development the installed capacity of water wheels might amount to 8 million horsepower or more. The latter figure may be compared with the installed capacity of water wheels in plants of 100 horsepower or more in the whole United States, which at the end of 1926 amounted to 11,721,000 horsepower.

Some of the large rivers in Oregon for which recent estimates have been made by the Geological Survey are listed below; the figures are based on the flow available 50 per cent. of the time. The figures for the Columbia River and the Snake and Klamath River Basins represent only Oregon's share of the resources of these rivers:

	Horsepower
Columbia River	1,408,000
Klamath River Basin	132,000
Umpqua River Basin	561,000
Rogue River Basin	532,000
Snake River Basin	823,000
Deschutes River Basin	734,000

In its work of classifying the public lands, as provided by law, the Geological Survey is collecting detailed information concerning the agricultural and mineral character and power-site value of every tract of public land and thus obtaining a mass of information concerning natural resources that is of great value to the States containing these lands. In Oregon, for example, the Klamath, Rogue, and Umpqua Rivers have been described in water-power reports made public in manuscript form. The power and irrigation resources of Deschutes River are described in Water-Supply Paper 344.

Many of the maps of the rivers of Oregon have been published by the Geological Survey in its regular water-supply papers and others are published as river-survey maps. The sections of rivers covered by these surveys made before 1927 are listed in Water-Supply Paper 558.

The manuscript reports on the water-power resources of Oregon and the maps of its rivers may be consulted at the office of the Geological Survey, in Washington, D. C.

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